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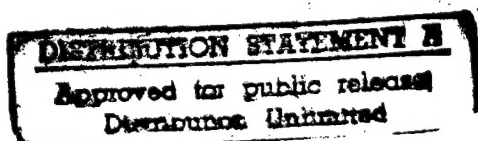
**2nd INTERNATIONAL SYMPOSIUM**

**MOLECULAR ORDER AND MOBILITY  
IN POLYMER SYSTEMS**



May 21-24, 1996  
Saint-Petersburg

**BOOK OF ABSTRACTS**



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**2<sup>nd</sup> INTERNATIONAL SYMPOSIUM  
MOLECULAR ORDER AND MOBILITY  
IN POLYMER SYSTEMS**

Saint-Petersburg, May 21-24, 1996

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# INTERPRETATION OF PREFERENTIAL ADSORPTION USING RANDOM PHASE APPROXIMATION THEORY

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The random phase approximation theory ( R.P.A.) can be used for system with any number of components and it is interesting to study the difference between its results and the virial expansion which has been used extensively for studying three components systems (one polymer and two solvents). In this paper we shall focus the discussion on the problem of preferential adsorption. The comparison between the results obtained by Read in 1960 and the results of R.P.A.(which is valid in a much broader domain) show that the differences are not very important at low concentration if one defines correctly the difference between the intensity scattered by the dissolved polymer and the solvent mixture . The effect which requires to correct the molecular weight is much more a geometrical effect than a thermodynamical one. Anyway at high concentration the effect becomes more or less negligible.



# Ground-State Approximations for Adsorption from Multicomponent Polymer Solutions

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A simple ground-state approximation (GSA) is used to calculate the composition of an adsorbed layer in a multicomponent solution of homopolymers. The model uses two basic assumptions. The first is that the volume fraction at position  $z$  of a component with chain length  $N$  can be written as the product of the square of an eigenfunction  $g(z)$  and the  $N$ -th power of an eigenvalue  $\lambda$ . The second is that only segments in contact with the surface experience a field  $u$  which is different from that in the bulk solution: only for these segments the segmental weighting factor  $G=\exp(-u)$  differs from unity. Then  $g(z)$  can be shown to decay exponentially. A simple relation between  $G$  and  $\lambda$  is derived from the boundary condition for  $g(z)$  at the surface. For a given adsorbed amount of a component with chain length  $N$ ,  $\lambda$  can be computed directly. In a multicomponent mixture where only the total adsorbed amount is given, the mass balance is needed;  $L$  now has to be solved from an implicit equation. More in general, this equation does include explicitly the excluded volume in the surface layer. The contribution of each chain length in a mixed adsorbed layer is obtained by weighting again with the  $N$ -th power of  $\lambda$ .

This approximate model gives results which are in excellent agreement with numerical self-consistent-field calculations. Several examples are given to illustrate the applicability of the model to experimental systems: adsorption fractionation in polydisperse polymers, polymer-polymer displacement, and adsorption and desorption isotherms in polydisperse systems. Simple expressions are obtained for the chain length characterising the transition between (long) adsorbed and (short) non-adsorbed chains, and for the width of the transition zone.

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# MOLECULAR MOBILITY AND ORDERING OF IONIC SURFACTANT IN OPPOSITELY CHARGED POLYELECTROLYTE GELS

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Cooperative reaction of lightly cross-linked polyanions (polycations) with oppositely charged cationic (anionic) surfactants resulting in polymer-surfactant complexes (PSC) stabilized by Coulombic and hydrophobic interactions were studied. Sorption of ionic surfactant molecules by oppositely charged network proceeds via their active transport into the gel phase. The driving force for the transport is produced by the reaction proceeding between the fragments of the network and surfactant ions at the solution-gel interface. The PSC composition depends on the degree of dissociation of polyelectrolyte and surfactant but does not depend on the composition of polyelectrolyte-surfactant mixture. Surfactant ions are nonuniformly distributed in the products of incomplete reactions. Actually surfactant sorption is accompanied by the local collapse of those regions of the network which are converted into PST. As a result the sharp boundary between collapsed and highly swollen fraction of a gel appears. The phenomenon of "localized collapse" opens new possibilities for the design of core-shell type structures.

Structure of PSCs was studied by means of wide and small-angle X-ray scattering and DSC. The complexes were shown to include surfactant lamella attached to the oppositely charged cross-linked polyelectrolyte via electrostatic interaction. Within these lamella aggregates aliphatic radicals of surfactants of a sufficient length (14-16 carbon atoms or more) produce a crystalline hexagonal structure. Moreover the interaction of cross-linked polyelectrolytes with such surfactants results in formation of spontaneously oriented PSC phase. That was proved by observing the corresponding textures on the small-angle X-ray diffraction patterns.

## **POLYSOAPS: CONFIGURATIONS AND ELASTICITY**

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By incorporating surfactants into flexible chains, we arrive at an interesting, little explored, class of materials: Polysoaps. These comprise of a water soluble backbone incorporating, at intervals, covalently bound amphiphilic monomers. In water, the polymerised amphiphiles self assembled into micelles of various geometries. This induces a dramatic modification of the spatial configurations of the polymers. What were featureless random coils now exhibit intramolecular, hierarchical self organisation. Due to this self organisation it is necessary to modify the description of the large scale behaviour of these polymers: Their configurations, dimensions and elasticity. Understanding the behaviour of these polymers is of practical interest because of the wide range of their industrial applications, ranging from cosmetics to paper coating. It is of fundamental interest because polysoaps are characterised by a rugged free energy landscape that is reminiscent of complex systems such as proteins and glasses. The talk concerns theoretical arguments regarding the following issues: (i) The design parameters that govern the spatial configurations of the polysoaps, (ii) The interaction between polysoaps and free amphiphiles, (iii) The effect of the intramolecular self organisation on the elasticity of the chains.

# ABC AND BAC TRIBLOCK COPOLYMERS - MORPHOLOGICAL ENGINEERING BY VARIATION OF THE BLOCK SEQUENCE

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In comparison to AB diblock copolymers ABC triblock copolymers display many more morphologies. Besides the composition and the different binary interactions as expressed by segmental interaction parameters, the sequence of the blocks (ABC, BAC) may be used as an additional structural variable. The different blocks may tend to form differently shaped microdomains which may lead to microphase separated morphologies with or without long range order. This will be discussed on the example of polybutadiene-block-polystyrene-block-poly(methyl methacrylate) triblock copolymers. While in the case of diblock copolymers mainly transitions between an ordered microphase separated morphology and the disordered homogeneous melt are known, ABC triblock copolymers show a larger variety of possible microphase transitions. The systems may undergo partial mixing of two of the three blocks when moving from the demixed to the homogeneous melt. The phase transitions depend not only on the composition of the triblock copolymers, but also strongly on the sequence of the different blocks. Model calculations show that mixing of the end blocks is enhanced by a phase separated middle block, while a phase separated end block hinders the mixing of the other end block with the middle block. The qualitative prediction of the model calculations are compared with experimental results on poly(ethylene-alt-propylene)-block-poly(ethyl ethylene)-block-polystyrene triblock copolymers and their corresponding diblock copolymers without a styrene block. Here miscibility of the two elastomeric blocks occurs when the temperature is elevated, while the styrene block stays phase separated from the elastomeric blocks.

## Acknowledgement:

This work on ABC triblock copolymers is the result of the engagement of a number of graduate students and postdocs: C. Auschra, V. Balsamo, J. Beckmann, U. Breiner, S. Brinkmann, E. Giebeler, F. v. Gyldenfeldt, U. Krappe, D. Loveday, H. Hueckstaedt. The theoretical work has been done in collaboration with L. Leibler; I. Ya. Erukhimovich contributed in many discussions. Electron microscopy is done in collaboration with R. Wuerfel (group of I. Voigt-Martin). The work is made possible by financial support from BMBF/BASF; Stiftung Innovation Rheinland-Pfalz, DFG, FdCh.

## NEW PROPOSALS FOR ARTIFICIAL MUSCLES

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Gels can be strongly swollen by external agents, but this mechanical response is not very practical for various reasons (a) the transition between compact and swollen states involves very strong local tensions and damages the sample (b) since solvent must diffuse in or out, the response times are limited by diffusion, and are very slow. We propose here a set up which would, to some extent, eliminate these difficulties. It is based on a network with a nematogenic backbone, swollen by a nematic solvent, with molecules very similar to the backbone. Then a slight drop in temperature (from the isotropic to the nematic regime) could induce a strong uniaxial deformation, with nearly 0 volume change.

# ELECTROOPTICAL PROPERTIES OF MESOGENIC CHAIN MOLECULES IN SOLUTION AND IN NEMATIC STATE

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Electrooptical characteristics of mesogenic chain molecules in solution and in mesophase can be described in terms of intra- and intermolecular orientational orders. The value and sign of electric birefringence  $\Delta n$  (EB) in a solution of kinetically rigid chain molecules are determined by the combination of two factors: intramolecular orientational order which depends on the dipolar and anisotropic architecture of the molecule and intermolecular orientational order caused by the action of the external electric field  $E$ . The value and sign of the dielectric anisotropy  $\Delta\epsilon$  of the polymer nematic phase are also determined by the combination of intra- and intermolecular orders. However, in this case the latter is not maintained by the external field but by the nematic potential of the mesophase. Therefore, comparative investigations of electrooptical properties of polymers in solutions and in nematic melts make it possible to obtain information about the intra- and intermolecular orientational orders of the molecules under investigation in these two states. These investigations were carried out using the EB method in solutions and the method of orientational deformations of nematic textures in an electric field. The objects being investigated were nematogenic dimers and trimers. Experimental data obtained for these compounds showed the presence of intramolecular order in their molecules, which is manifested in the odd-even oscillations of the value and sign of Kerr constant  $K \approx \Delta n/E^2$  in solution and  $\Delta\epsilon$  in the nematic phase when the number of C-C bonds in the methylene spacers of these molecules is varied. This effect is particularly dramatic in the mesophase where it is enhanced by intermolecular nematic potential.

This work was supported by the Russian Foundation of Fundamental Investigations (grant 96-03-33863a).

# **DYNAMICS AND PIEZOELECTRICITY IN POLYMERIC AND ELASTOMERIC FERROELECTRIC LIQUID CRYSTALS**

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2D-IR-Spectroscopy, Broadband Dielectric Spectroscopy and Michelson-Interferometry are employed to study the dynamics and the piezoelectricity of polymeric and elastomeric ferroelectric liquid crystals. The samples being obtained in thin and ultrathin layers are macroscopically oriented. Its dynamics takes place in a frequency windows between  $10^{-4}$  Hz to  $10^{10}$  Hz. Huge (inverse) piezoelectric effects are observed offering completely new routes for innovative applications.

# **SCATTERING METHODS FOR THE STUDY OF MORPHOLOGY AND PHASE TRANSITIONS IN CRYSTALLINE AND LC POLYMERS**

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Scattering, using light, x-rays, and neutrons serves as a probe for polymer morphology and its changes with phase transitions and orientation. The wavelength of the radiation selected must be commensurate with the structural features being studied. A case which will be emphasized in the presentation will be the study of the miscibility and crystallization of polyethylene blends. Small-angle light scattering serves to characterize spherulite size. Through joint application of Hv and Vv polarization modes, it is possible to also determine the numbers of spherulites and their anisotropy which is related to their degrees of crystallinity. These measurements may be combined with real-time small-angle x-ray scattering and x-ray diffraction studies so as to simultaneously follow degrees of crystallinity and lamellar thicknesses. Changes are also followed during melting and it is shown that such measurements can establish whether or not melts were phase separated.

Small-angle neutron scattering can be employed using deuterium-labeled components or portions of molecule to establish their morphological role.



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## **Conformational Transitions In Macromolecules of Complex Chemical Structure During Liquid Crystalline Ordering**

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The reported research was conducted in order to check theoretical predictions about changes in conformational order in macromolecules of thermotropic polymers during their transition into liquid crystalline (LC) state and to link these changes with real chemical composition of macromolecules. With this objective in view three following types of thermotropic polymers with complex chemical structure were investigated:

- linear and combined (with mesogen in both main and side-chains) polymers, containing malonic acid fragment (MAF) in the main-chain;
- linear polyesters with possibility of conformational isomerism in mesogen, containing 3,3'-azobenzene (AB)-substituted unit in the center of mesogen;
- linear aperiodic main-chain copolymers with the same type of mesogens and spacers of variable lengths or composition.

It was shown that conformation of macromolecules of polymers of the first type in LC state is determined by the most advantageous conformation of MAF (with minimum of energy). As a result main-chain of these polymers in the LC state have a hair-pin conformation (in contrast to extended chain conformation for main-chain polymers, containing methylene groups in spacer). This type of main-chain conformation determines specific macrocharacteristics of these class of polymers.

For polymers of the second type it was demonstrated that in the LC state energy of activation of thermo-isomerization reaction (cis- to trans- transition on AB unit) changes in comparison with isotropic melt in a way, favorable for the more extended conformation of mesogen with trans-configuration of AB unit. Irradiating samples of this polymer type by UV-light it was shown that the presence of up to 40% of cis-form of AB unit does not lead to the loss of LC properties of melts but does induce widening of biphasic region in the vicinity of nematic-to-isotrop transition. This effect of widening may be connected with heterogeneity of chain composition of irradiated polymers.

For the last type of polymers it was found that there are two different ways for formation of smectic LC order: segregation of fragments with different chemical composition or conformational changes in spacer, accompanied by such changes in spacer's lengths that coaxiality of mesogens is preserved. Number of defects in layer's structure in the latter case depends on difference in spacers' lengths, their chemical composition and asymmetry value of mesogen.

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## VIGNETTES IN POLYMER DYNAMICS

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Several distinct topics are discussed: (1) Mobility of poly(fluoromethylene) and other fluorinated ethylene polymers as revealed by NMR spin-lattice relaxation data is quite high, refuting the still commonly held view that fluorocarbon chains are "stiff;" (2) the fractional-power viscosity dependence of segmental motions is easily rationalized by simple free-volume considerations of the Cohen-Turnbull type; (3) the so-called "transitions" of the T11 type popularized by Boyer and others can be explained as due to rather broad shifts in conformational equilibria, and require no special mechanisms.

# CHAIN MOBILITY AND CRYSTAL FORMATION: A NEW APPROACH TO POLYMER CRYSTALLIZATION WITH WIDER IMPLICATIONS

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Molecular mobility in the crystalline state is a long recognized topic of interest. Nevertheless the existence of mesophasic 'mobile' crystal phases creates altogether new perspectives. Such a phase has been recognized originally in polyethylene in the form of a hexagonal phase traditionally realizable as the stable phase at elevated pressures, and subsequently also found at atmospheric pressure in suitable substances such as poly 1-4 trans butadiene and symmetrically long-alkane substituted siloxanes. In all such cases the high chain mobility results in extended chain type crystals. However, latest works (1,2), currently centred on polyethylene, reveal that such crystallization in a mobile phase is not restricted to the special cases listed above but can be a precursor stage in the more conventional chain folded crystallization in the traditional 'true' crystal phase thus affecting, or rather widening our present conceptions in the subject of polymer crystallization.

The principal conception underlying it all is the size dependence of phase stability in the form of 'phase stability diagrams' in the light of which a mobile phase, metastable for infinite size, could become the stable one at the small sizes pertinent at the stage when the crystal nucleates and starts to grow. Such growth then takes place both laterally and also in the thickness direction (the newly defined 'thickening growth' (3) the latter being terminated on transformation into the crystal phase of ultimate stability. Thus this transformation 'locks in' the crystal thickness at which the transformation occurs, which, accordingly, provides a new hitherto unsuspected source for the lamellar thickness (the fold length) of the traditional chain folded crystal. The relation of the new picture to the one envisaged so far for chain folded crystallization will be laid out and some totally new aspects of crystal growth while in the mobile phase (4,5) involving sliding diffusion (6) will be presented.

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## **Thermodynamics of stationary fluctuations in liquids - the conformon model**

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The thermodynamics of fluctuations in liquids is developed in terms of the conformon model. Predictions of the model are proven by many experiments (specific heats, thermal expansion of liquids). From the universal behavior of the fluctuations in liquids it results that glass-formers - independent on the type of molecules they are comprised of - show altogether the same reduced energy-density of the fluctuations at the quasi-static glass-transition temperature. The fluctuations and the global structure in liquids of all glass-forming systems - low molecular weight and polymer systems (networks included) - should exhibit the same features (also of the disordered structure) provided that they are related to the glass-transition temperature. Some consequences of this symmetry are presented in the talk.

The above examples include a characterization of the disordered structure in the glassy state revealing that one of the possible conformon configurations realized in the supercooled liquid is frozen in. The general features of the global structure of glasses is shown to be invariant down to very deep temperatures. Despite of the different kinetics in the regime of about 1 K (tunnelling processes!) the relaxation-mode distribution is found to be the same as the one used for describing the relaxation in the glass-transition regime. General consequences will be discussed in the talk.

At the end, newest results - obtained with the aid atomic-force microscopes - are presented. These measurements allow to prove the basic assumption of the conformon model that liquids should exhibit stationary modes of finite size and finite life time the existence of which makes the momentary structure "heterogeneous". This is most impressively documented by investigations of mono- and di-layers of "bottle-brush" molecules.

In view of these results our general understanding liquids is finally reflected. It seems to hold true that liquids (and also glasses) exhibit outstanding universal dynamic and structural features typifying them in a unique manner irrespective of the molecules they are comprised of.

## **Chain Reorientation in PTFE by Mobile Twin Helix Reversal Defects**

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Scattering experiments with electrons, X-rays and neutrons, together with vibrational spectroscopy, carried out on biaxially oriented samples of PTFE indicate that the dominant mechanism of motion in the intermediate and the high temperature phase is a reorientation of the chain units effected by the formation and motion of twin helix reversal defects. In contrast to single helix reversal defects, twin defects constitute a truly local perturbation, with solitonic dynamic properties. One species, the 'coherent twin defect', retains the long-range order along the chain and therefore possesses a particularly low activation energy. The defects mainly form in the intermediate phase; in the high-temperature phase, saturation occurs. The observation suggests for the intermediate phase a control by both intra- and intermolecular potentials whereas in the high temperature phase the intermolecular forces are smeared out. Twist long-range order is preserved through the intermediate phase, with a continuous decrease with temperature. The transition to the high temperature phase is accompanied by a break-down of the remaining long-range order. In spite of the complete loss of twist long-range order at elevated temperatures, monomer units

# **MOLECULAR ORDERING IN HYDROPHILIC POLYMERS SOLUTIONS IN CONNECTION WITH TARGETED TRANSPORT**

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Aqueous solutions of polyacrylamide family polymers having LCST have been studied. Structural investigations using model compounds and modified acrylamide polymers above and below LCST led to certain conclusions about conformational peculiarities and type of non-covalent interaction in these systems.

Linear polymers LCST around 37°C have been used for chemical immobilization of some pharmaceutically active compounds and biological activity of these systems at temperatures below and above LCST was studied. It was shown that phase transition at LCST results in temperature driven transport of macromolecular species and that of active drugs into desirable and regulated spot of closed system.

# **POLYELECTROLYTE SIMULATIONS: FROM SINGLE DEBYE HÜCKEL CHAINS TO SOLUTIONS**

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The talk will shortly review work on single weakly charged polyelectrolytes as well as simulations on solutions of strongly charged chains. For the first case [1] a model system with Debye Hückel potential for the electrostatic interaction and harmonic bond potentials, modelling the neutral chain in between the charges, is considered. We find that the persistence length neither follows a  $\Gamma^{+2}$  ( $\Gamma$  the Debye length) nor a  $\Gamma^{+1}$  power but is sublinear in  $\Gamma$ . For the solution simulations [2] up to 2048 charged particles (monomers and counterions) could be taken into account to study the conformational properties as a function of density and Bjerrum length. None of the currently discussed theoretical pictures can fully account for the simulation findings.

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## **Chain Conformations, Dynamics, and Interfacial Properties of Polymer Melts from Atomistic Molecular Dynamics Simulations**

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Molecular dynamics simulations of polymer melts of reasonable chain lengths can now be performed with a reasonably good representation of atomistic architecture to compute the full equilibrium and dynamic properties, by taking advantage of powerful parallel computational methods. Moreover, reliable information on the geometries and energy profiles on model molecules can now be obtained from high-level ab initio quantum chemical calculations, so that they provide the means to derive accurate force fields for a variety of real atomistic repeat structures. Recent investigations of such atomistic simulations include: (1) the condensed-phase effects on chain conformations, (2) local chain dynamics and monomer friction, and (3) the surface structures and surface tension of polymer melts.

For example, we have found that the Flory's picture of unperturbed random-coils in polymer melts is very accurate for polymethylenes, but fails for poly(oxyethylene) owing to the presence of significant conformation-dependent intermolecular (polar) attractive interactions. We have delineated the details of local motions in polymethylene and poly(oxyethylene) melts in good agreement with results of NMR and dielectric relaxation experiments, and investigated their relevance to monomer friction constants. We also derived the surface tension of polymethylenes in good agreement with experimental values, and successfully demonstrated how the perfluorination to poly(tetrafluoroethylenes) significantly changes the P-V-T relationship and the surface tension.



# STATIC AND DYNAMIC LIGHT SCATTERING STUDIES OF POLYMER MELTS AND SUPERCOOLED LIQUIDS

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As it is now well established, glass forming organic liquids and polymers exhibit long range density fluctuations with correlation length  $\xi$  in the range of 10 - 200 nm. A summarizing review of the relevant experimental observations is presented.

The inhomogeneities of the free volume distribution on this length scale give rise to some unexpected features, which cannot be explained on the basis of conventional liquid state theory. Especially an ultra slow hydrodynamic mode (relaxation rate  $\Gamma \sim q^2$ ) is detected with  $\Gamma$ 's about  $10^{-6}$  to  $10^{-9}$  times smaller than those of the usual primary  $\alpha$ -process. In addition, the static light scattering intensity  $I(q \rightarrow 0)$  is no longer proportional to the isothermal compressibility and shows a strong  $q$ -dependence.

In order to explain these observations at least qualitatively, a two-state model is proposed, which starts from the coexistence of "liquid like" and "aperiodic solid like" regions within the liquids. The molecules in the different dynamic states aggregate during equilibration and form extended clusters, which cause an excess light or small angle X-ray scattering intensity. The ultra slow mode reestablishes the ergodicity of the systems.

## PHASE TRANSITIONS IN POLYMER BRUSHES

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Polymer brushes immersed in a solvent can undergo phase transition from swollen to collapsed state due to the change of external conditions (solvent quality, temperature). The peculiarities of such transitions are closely connected with inhomogeneity of segments distribution inside the brush.

The simplest box-like model of the planar brush can give only jump-like "all-or-none" phase transition. According to the theory, the necessary condition for the phase transition in this model is the existence of specific groups in the chains forming the brush. That are charged groups of polyelectrolyte chains or mesogenic groups with orientationally dependent interactions.

The theory with account of the brush inhomogeneity predicts for brushes with specific groups the phase transition from the swollen to the microphase segregated state. Two sublayers coexist in this state. The intrinsic sublayer shows up as a collapsed brush (with high orientational order in the case of mesogenic segments). It is separated by interface boundary from the external swollen sublayer.

The phase transitions induced by normal deformations of the brushes are also investigated.

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# **INTERFACES BETWEEN COEXISTING PHASES OF POLYMER MIXTURES: COMPARISON BETWEEN MONTE CARLO SIMULATIONS AND THEORETICAL PREDICTIONS**

**Kurt Binder and Marcus Müller\***

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Large scale Monte Carlo investigations of the interface between A-rich and B-rich phases of symmetric binary (AB) polymer mixtures are presented, using the bond fluctuation model of flexible chains with  $N_A=N_B=N=32$  effective monomers. The temperature range studied,  $0.144 < T/T_c < 0.759$ , includes both the strong and the weak segregation limits. Interfacial free energy and interfacial structure are studied, and compared to predictions based on the selfconsistent field theory. Also the broadening of the interfacial width due to capillary waves is considered, and finite size effects due to the confinement of interfaces in thin films of polymer blends are discussed.

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## STRUCTURE OF ADSORBED POLYMER LAYERS

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We discuss the structure of polymer layers adsorbed from a dilute solution onto a solid surface using both a scaling approach and a mean field theory.

In the scaling approach, the adsorbed polymer is shown to have a double layer structure with an inner layer essentially formed by loops (chains segment starting from the surface and ending on the surface) and an outer layer formed by tails (the endchain segments starting on the surface and with a free end point in the solution). We present a new analytical mean field theory for polymer adsorption that explicitly considers tails and loops. This theory allows a precise determination of the monomer concentration profile which shows a very good agreement with the numerical work of Schjeutens and Fleer. This mean field model is used to study the interaction between adsorbed polymer layers and the adsorption of polymers with various architectures (combs, stars, rings).

# MORPHOLOGIES OF CREW-CUT AMPHIPHILIC BLOCK COPOLYMER AGGREGATES IN AQUEOUS SOLUTIONS

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It was shown before that highly asymmetric diblock copolymers in solution can self-assemble to yield aggregates of various morphologies. Depending on the block copolymer composition, the aggregates can be regular small spherical micelles, cylindrical micelles, vesicles or lamellae, and large compound micelles, LCM's, consisting of packed reverse micelles but with a hydrophilic surface. More recently, it has been found that aggregates of various morphologies can also be produced from polystyrene-*b*-poly(ethylene oxide) diblocks, PS-*b*-PEO, again involving different compositions. By contrast to the behavior of the PS-*b*-PAA system, the large compound micelles are found in the sample with higher PEO content. Coexisting multiple morphologies are seen frequently in the PS-*b*-PEO system.

It is also shown that the morphology of the crew-cut aggregates can be controlled via the addition of micro-molar ( $\text{CaCl}_2$  or  $\text{HCl}$ ), or milli-molar ( $\text{NaCl}$ ) concentrations. In addition to spherical, rod-like and uni-vesicular or lamellar aggregates, large compound vesicles (LCV's), a new morphology, can be obtained from a single block copolymer. Gelation of a dilute spherical micelle aqueous solution can also be induced by ions due to the formation of a cross-linked "pearl necklace" morphology, an intermediate step toward rod formation, with the gel held together by multifunctional beads. The morphogenic effect of added ions at such low concentrations on block copolymers is believed to be novel.

## SPREADING OF POLYMER MOLECULES ON SOLID SURFACES

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During an adsorption event, a linear chain arriving from solution first makes contact with the substrate and then undergoes a kind of spreading process to achieve the optimum number of polymer/surface contacts. This spreading process has been considered from a theoretical point of view, but here we shall mainly discuss experimental data from which spreading rates can be inferred.

We first note that, in equilibrium and on an empty surface, polymers spread to a larger extent than on a surface carrying a dense, crowded adsorption layer. During the build-up of an adsorption layer, two time scales play a role, the spreading time and the build-up time of the adsorbed layer. If the latter is the longest, the surface chains can be considered as relaxed throughout the adsorption process; they always spread to the extent corresponding to the surface coverage. In the opposite case, the chains spread very little, so that large loops are formed. The surface coverage can therefore be much higher. In the special case that both times are approximately equal, a layer of densely packed chains with a small degree of spreading initially forms. Subsequent further spreading should then drive off the excess polymer and the kinetic curve has an overshoot. In experimental situations it is possible to vary the build-up time of the adsorbed layer to some extent. In the majority of cases, however, the adsorption kinetics do not change detectably, meaning that the spreading occurs much faster. However, recent experiments with the polysaccharide dextrane adsorbing onto a metal oxide surface have shown a remarkably large effect of the (final) surface coverage on the layer build-up time. No overshoot was found, though, implying that the spreading (which does occur on the empty surface) was completely blocked by the presence of other chains on the surface.

Indeed, competitive spreading (spreading at the expense of surrounding chains) is rather different from spreading of a single chain. In particular, if the spreading chain and its competitors are chemically identical, the adsorption of one chain at the expense of a neighbouring one is likely to be a kind of defect diffusion process, not unlike reptation; the "defect" in this case is a broken segment/surface bond.

The competitive adsorption experiment can be advantageously used for monitoring spreading rates, by means of the desorption they bring about. We shall discuss cases of chemically identical chains (differing in length only) as well as chemically different chains, where the difference in segmental adsorption energy provides an extra driving force for exchange. Various data will show that lowering the segmental adsorption energy enhances the rate of spreading. Hence, spreading is indeed an activated process, with the detachment of an adsorbed segment is a rate-determining step. To what extent chain stiffness plays a role is less clear.

## CRYSTALLINE ORDER AND ORIENTATION IN POLYMER FILMS

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Amorphous films of polyethylene terephthalate (PET) obtained by melt pressing and quenching with a thickness of 200  $\mu\text{m}$  were oriented by cold drawing and then crystallized. The orientation of the molecules was investigated by means of wide angle X ray scattering (WAXS), small angle X-ray scattering (SAXS) and deutron NMR. A preferential orientation of the chains in draw direction and of the 100 plane parallel to the film plane was found. The degree of orientation was highest in the crystals and for the taut amorphous chains and smaller for the highly mobile amorphous chains.

In another experiment much thinner (40 nm) amorphous films of PET were obtained by spin coating from a dilute solution in hexafluoroisopropanol onto silicon wafers or onto float glass. These films were crystallized. Before and after crystallization grazing incidence diffraction (GID) experiments were performed in vacuo employing synchrotron radiation. By varying the angle of incidence the scattering of sheets of different depth can be obtained. A significant orientation of the net plains was found which was strongly influenced by the spinning rate and the concentration of the solution. These orientations will be compared to the orientation found in the thick film and will be discussed.

Further GID experiments were performed on thin films of poly(ethylene oxide) (PEO). In this case the films obtained by spin coating were already crystallized. Again a characteristic orientation of the crystals was found.



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# SURFACTANT SELF-ASSEMBLIES IN POLYMER GELS

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The interaction of polyanionic and polycationic gels with oppositely charged surfactants is considered. It is shown that in this case the surfactants are effectively absorbed by the gels and form hydrophobic self-assemblies inside them. Simultaneously the gel collapses. The SAXS investigation of the organization of hydrophobic surfactant aggregates inside the gels reveals an extremely high degree of spatial order. Aggregates form a regular superlattice which spans over several hundred of nanometers, while the size of the aggregate and the mesh size of the gel is of order several nanometers. Surprisingly enough, the medium of statistically disordered gel is shown to promote the long-range order in the superlattice of aggregates: the well-organized aggregates are more easily formed within the gels than in pure water solutions (at equal concentrations of surfactants). The interaction of gel/surfactant complexes with metal ions, subsequent reduction of these ions and the formation of metal nanoparticles inside hydrogels are also considered.

# CONCENTRATION EFFECT ON THE DIELECTRIC NORMAL MODE RELAXATION IN THE TERNARY SYSTEM POLY ( $\epsilon$ -CAPROLACTONE)/ POLY(4-CHLOROSTYRENE)/DIOXANE

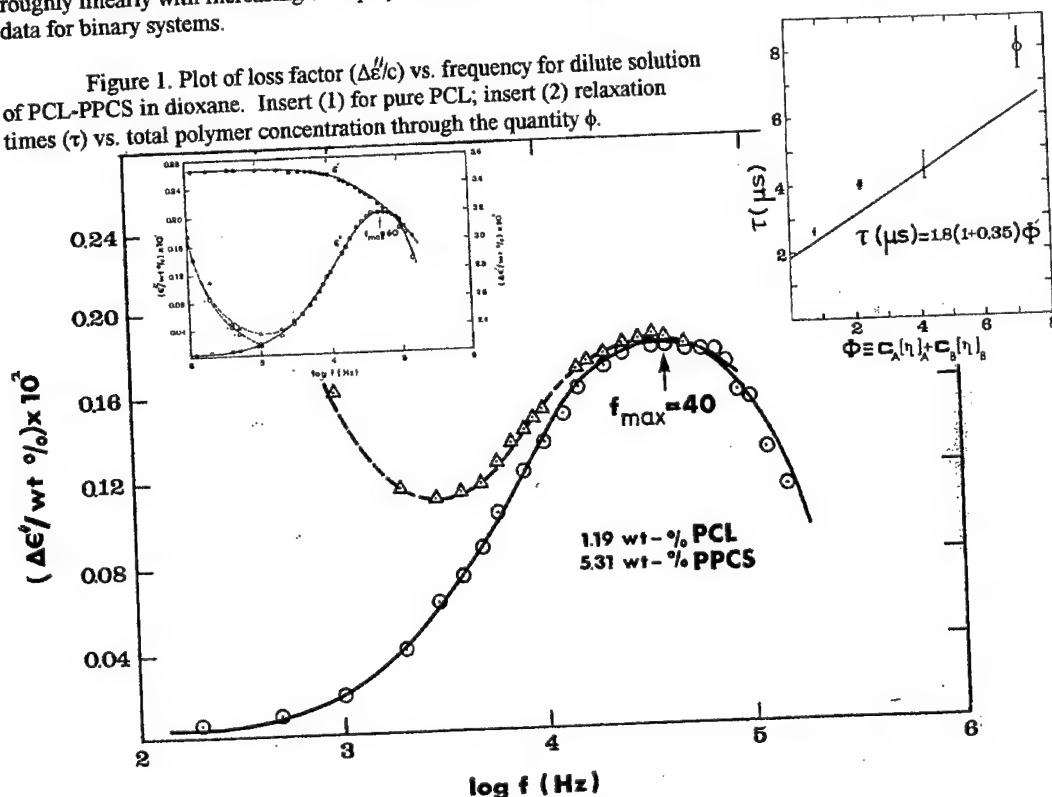
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The concentration dependence of the relaxation times of the internal normal modes of linear chains in polymer solutions provides information on hydrodynamic interactions.

Solutions of poly( $\epsilon$ -caprolactone) in dioxane display dielectric dispersion in two distinct frequency region, one of which in the low-frequency range shows strong molecular weight dependence. The low-frequency loss peak can be attributed to a component of the repeat-unit electric dipole moment parallel to the direction of the chain backbone.

In this work dielectric permittivity has been measured for some ternary mixtures of poly( $\epsilon$ -caprolactone), poly(4-chlorostyrene) and dioxane at 25°C. The three components exist in this system were miscible with each other. In addition to the novelty of the experiment, it has the advantages of introducing no additional ionic conductance, such as plagued the measurements on poly( $\epsilon$ -caprolactone), and of minimizing interference due to the dielectric loss of the poly(p-chlorostyrene), which lies at much higher frequencies. The relaxation time due to the longitudinal component of the ester-group dipole in the polyactone chain increases roughly linearly with increasing total polymer concentration at a rate in rough agreement with earlier dielectric data for binary systems.

Figure 1. Plot of loss factor ( $\Delta\epsilon''/c$ ) vs. frequency for dilute solution of PCL-PPCS in dioxane. Insert (1) for pure PCL; insert (2) relaxation times ( $\tau$ ) vs. total polymer concentration through the quantity  $\phi$ .



# STOICHIOMETRY, STRUCTURE AND STABILITY OF POLYELECTROLYTE COMPLEXES

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Polyelectrolyte complex (PEC) formation represents a simple but very interesting principle of structure formation with high practical relevance (e. g. flocculants, coatings, membranes with special separation properties, microencapsulation). In most applications PEC formation is carried out under conditions, which lead to highly aggregated systems, often to macroscopic flocculation. While soluble PECs on a molecular level were comprehensively studied by Tsuchida and Kabanov [1, 2], a complete understanding of the processes, governing the formation and properties of the higher aggregated structures are still missing. Complex formation between polyanions and polycations with strong ionic groups and/or comparable high molecular weight results in such structures. The degree of aggregation is mainly controlled by the concentration of component solutions [3]. In highly diluted solutions (<10<sup>-4</sup> g/ml) quasi-soluble particles on a colloidal level are formed, which can be studied by all methods, normally used in polymer characterisation. Previous studies by UV/VIS spectroscopy, potentiometry, viscosymetry, static and dynamic light scattering as well as electron microscopy showed that e. g. PECs between Na-poly(styrenesulfonate) and copolymers of acrylamide and diallyldimethylammonium chloride of various compositions exist at non-stoichiometric mixing ratios as highly polydisperse systems of compact and nearly spherical particles, which are stabilised by an excess of the major component [4]. The degree of swelling increases with rising content of acrylamide in the polycations. The main objective of this contribution consists in the investigation of the salt stability of such PECs, studied by static light scattering and UV/VIS spectroscopy. A detailed analysis of the scattering curves provides comprehensive information about the structure changes caused by addition of NaCl.

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## **DIBLOCK COPOLYMER NANOSTRUCTURES**

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Polystyrene-block-poly(2-cinnamoyl ethyl methacrylate) (PS-b-PCEMA) of different block lengths, where PCEMA is photocrosslinkable block, was synthesized. These polymers self-assembled in THF/cyclopentane mixtures to form micelles with PCEMA as the core. Depending on the relative length of PS to PCEMA, the micelles can be star and crew-cut ones. At a solid and solution interface, the polymers assembled to form polymeric monolayers called polymer brushes. In the bulk, the two blocks phase segregated to have spherical, cylindrical, and lamellar domain formation from the PCEMA block.

The self-organized structures were then irradiated to crosslink the PCEMA block. Irradiation of star and crew-cut micelles crosslinked their cores to produce star polymers and nanospheres, respectively. Irradiation of polymer brushes yielded chemically more stable polymeric monolayers. Nanofibers and nanoplates were each prepared by dissolving irradiated PS-b-PCEMA films with cylindrical and lamellar PCEMA domains.

In addition to my discussion of nanostructure preparation, this presentation will also address the size control of these nanostructures.

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# MICROPHASE STRUCTURES IN NOVEL MACROMOLECULAR ARCHITECTURES OF BLOCK COPOLYMERS

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The synthesis of novel non-linear block copolymers of the  $A_2B$  (3-miktoarm star copolymers),  $A_3B$  (4-miktoarm star copolymers),  $(AB)_2(BA)_2$  (inversed 4-miktoarm star block copolymers),  $A_8B_8$  (16-miktoarm star copolymers),  $(BA)_{n=2,3}B$ ,  $A_3BA_3$  (bridged miktoarm star copolymers) and  $(BA)_3B(AB)_3$  type was achieved. A is polyisoprene (PI) and B polystyrene (PS). The synthetic approach involves the controlled reaction of the appropriate chlorosilane with monofunctional or difunctional macroanions of B, followed by addition of the monofunctional macroanion A or BA. Characterization carried out by size exclusion chromatography, low angle laser light scattering, laser differential refractometry, membrane and vapor pressure osmometry, and NMR and UV spectroscopy indicated that these new materials have a high molecular and compositional homogeneity.

The microphase separation was studied by transmission electron microscopy and small angle x-ray scattering. Comparison with the corresponding linear block copolymers, showed that the macromolecular architecture not only affects strongly the morphological domain borders but it can introduce new morphologies as well.

# METASTABLE MESOPHASES

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Mesophases in the form of liquid crystals and condic crystals are important for the description of the phase structures of many linear macromolecules. The mesophases are characterized by a reduction in order relative to a crystal [1] and by the presence of large-amplitude molecular motion in the form of translation, rotation, or conformational mobility (internal rotation). For macromolecules, conformational motion is always the overriding large-amplitude motion. All mesophases that can be kept from full crystallization show on cooling a glass transition to a mesophase glass [2,3]. It is well known that melts do not supercool when forming liquid crystals, while the formation of crystals and condic crystals of macromolecule is always coupled with substantial supercoolings, typically 5 to 30 K [1]. A metastable liquid crystal may be formed if its isotropization temperature is located between the melting temperature of the stable crystal and its supercooled crystallization temperature under the given conditions. Several of such monotropic, metastable liquid crystals of macromolecules have been described in the past.

The present lecture will show on the examples of drawn poly(ethylene terephthalate) fibers and gel-spun ultra-high molar mass polyethylene that there is another class of metastable condic crystals that is based on the earlier observed rigid-amorphous fraction in semicrystalline polymers [4]. Due to restriction of the motion in parts of the macromolecules that bridge between crystals, only a part of the noncrystalline phase undergoes a normal glass transition. The rest stays "rigid" to higher temperatures, sometimes up to the melting temperature of the crystals. This rigid-amorphous fraction can be assessed quantitatively by calorimetry. In fibers this metastable third phase becomes a mesophase. The deformation needed for fiber formation introduces the order of a mesophase on a nanometer scale. It will be shown to be important for the description of structure-property-processing correlations. The mesophase may be the actual load-bearing part of the fibers.

The order of a mesophase can also be introduced by formation of nanometer-scale amphiphilic liquid crystals that gain order by the formation of a phase boundary. In the well-known microphase-scale amphiphilic liquid crystals, known from block copolymers, the order in the immediate vicinity of the surface is dissipated leaving only a liquid-crystalline superstructure. In nanophase-separated macromolecules the lamellar superstructure can lead to an metastable mesophase that bridges the gap between amphiphilic and thermotropic liquid crystals. A typical example that will be discussed is poly(4,4'-phthalimidobenzoyldodecamethyleneoxycarbonyl) (PEIM-12).

## Acknowledgments

This work was supported by the Div of Materials Res., National Science Foundation, Polymers Program, Grant # DMR 90-00520 and Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp. For the U.S. Department of Energy, under contract number DE-AC05-96OR22464.984.

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## "GLASS TRANSITION OF MAIN CHAIN NEMATIC LIQUID CRYSTALLINE COPOLYESTERS"

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Main chain liquid crystal polymers (MCLCPs) are of particular interest for their ability to be molded into self-reinforced articles. This is a result of a characteristic of their nematic mesophase melt which enables the molecular axes of the polymer chains to follow the direction of the flowing melt. However, the level of crystallinity in MCLCPs is low and the crystallites only account for a minor proportion of the total material. The variation of the stiffness with temperature in the region below the melting point of the crystallites depends very much on the molecular segments in the noncrystalline regions. The purpose of this lecture is to focus on glass transition phenomena in MCLCPs.

A series of LC aromatic copolyesters was investigated by thermal analysis, optical microscopy, X-ray diffraction and dynamic mechanical analysis. Amorphous, isotropic samples were prepared either by casting from dilute solutions or by precipitation into a nonsolvent. Subsequent annealing permitted the development of nematic LC order, which persisted upon cooling to ambient conditions. The kinetics of ordering toward the nematic state were slow enough to permit partially ordered states (i.e., between isotropic and nematic) to be experimentally accessible. The transition from the metastable isotropic state to the equilibrium nematic state appeared to proceed first by a global ordering of the polymer samples via main chain segmental motions. Then, ordering was found to continue via local segmental dynamics in regions where chemical sequences are favorably disposed to align as a result of the global ordering. The ordering resulted in an increase in polymer density and glass transition temperature and a decrease in WAXD d-spacing, consistent with the more dense nature of the ordered nematic polymers.

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## Molecular Design of Chiral Smectic Liquid Crystals and Polymers

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Several series of ferroelectric side chain liquid crystalline polymers will be described in this presentation. Differential scanning calorimetry, optical polarizing microscopy and powder X-ray diffraction measurements were used to determine their thermal transitions and to analyze their anisotropic textures. Moreover, the dielectric measurements were used to analyze the molecular dynamics of ferroelectric liquid crystalline polymers. The influence of polymer backbones, flexible spacers, mesogenic cores and chiral end groups on the mesomorphic properties of the polymers was discussed. The most suitable liquid crystalline structures for the formation of chiral smectic C phase are those which consist of oligo(oxyethylene) spacer, chiral butyl chain length coupling with three to four phenyl rings of ester mesogenic cores. Moreover, the copolysiloxane as the polymeric backbone is quite helpful for lowering the viscosity of ferroelectric side chain liquid crystalline polymer system. The development of ferroelectric liquid crystalline polymers exhibiting a broad temperature range (about 200°C) of chiral smectic C phase including room temperature was achieved.

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## PHOTOORIENTATION OF COMB - SHAPED POLYMERS WITH MESOGENIC SIDE GROUPS

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Comb-shaped copolymers containing azobenzene moieties and mesogenic fragments have attracted much attention in the last few years. The interest in such kind of photochromic polymers is dictated by their unusual properties which may be reversibly changed by light illumination to produce the highly-oriented polymer films [1-4].

The first part of the talk is concerned with synthesis and study of a series of amorphous and liquid-crystalline (LC) comb-shaped polyacrylates and polymethacrylates containing cyanobiphenyl and azobenzene side groups with aliphatic and oxyethylenic spacers of different length.

General attention is spared to the consideration of the photooptical effects and to the origin of photoinduced birefringence in the photochromic copolymers synthesized. Azobenzene fragments are able to display a reversible *trans-cis* configurational changes due to an illumination by laser beam. Photochemical switching between the rod-like *trans*-isomers and the bend *cis*-isomers causes a perturbation of the side chain packing.

The reorientation process includes not only dye-containing, but also non-photochromic mesogenic groups changes in such a way that the long axes of the side groups and the electric vector of laser beam become perpendicular. As a result the optical properties of initial polymeric films are considerably changed - high values of optical anisotropy are induced both in the LC and the amorphous films.

The optical anisotropy induced by laser illumination in the polymer films can be changed reversibly by rotating of the plane polarization of the laser beam in respect to the film. Thus the light acts as the "regulated external field" permitting to control the orientation of the side chains of the photochromic comb-shaped polymers.

This research was supported by the Russian Foundation of Fundamental Research, (1996) and HCM Programme of the EC Commission (Contract ERBCITDCT 940602).

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**STUDY OF PHOTOINDUCED MOLECULAR  
REORIENTATIONS AND RELAXATION BY POLARIZED  
MICRO-RAMAN SPECTROSCOPY AND INDUCED  
BIREFRINGENCY IN POLYMERIC LIQUID CRYSTALS**

**Marco Fontana**

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Scienze 43100 Parma 1 Italy*

In this paper we report on a novel method to study molecular relaxation at the glass transition of a polymeric liquid crystal. The polymer, a polyacrylate with an azobenzene side chain, has phototropic behavior due to a photoinduced cis-trans transition in the azobenzene moiety. Using a pump laser, we induce a molecular reorientation in the illuminated area which leads to a well aligned nematic single domain both in the nematic and in the glassy phase. We follow this process and the ensuing relaxation after the pump laser is turned off in two ways: microscopically, through polarised Raman spectroscopy which is sensitive to local order; mesoscopically through monitoring the transmission through crossed polarizers in a polarizing microscope of the light of a small probe laser. The implications of our results on studies of the glass transition in polymeric glasses, and on possible applications of these materials to optical memory devices will be discussed.

## **Hydrodynamique unfolding of swollen and collapsed chains : stems and flowers**

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Under a constant flow velocity  $V$ , a flexible polymer (in steady state) is expected to display three types of conformations 1) unperturbed at low  $V$  2) "trumpet" : partially stretched, with certain scaling laws at intermediate  $V$  3) stem and flowers with a completely stretched portion (the stem) at high  $V$ .

As the quality of the solvent decreases from good, to  $\theta$  to bad solvent, we never find a first order transition, but always a progressive unfolding with these three regimes. For these three cases, we derive the scaling laws for the stretching versus the velocity of flows. For chains in bad solvents, one must introduce the surface energy of the globule, which overcome the elastic energy.

We also consider transients where starting from a completely stretched chain (the stem) the flow is abruptly suppress. The resulting decay law for the stem is of the Rouse type. Using DNA molecule suitably decorated by fluorescent dyes, we have been able to observe directly the relaxation under an optical microscope after complete stretching by a Poiseuille flow in a capillary vessel. The relaxation starts from the free ends, where flowers expand whereas the stem is progressively destroyed. We find that the size of the flower increases like square root of time, in perfect agreement with our theoretical model.

## **The mechanical and dielectric relaxation properties of polymer networks with interchain and external friction**

**Yu. Gotlib**

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In the most previous theories the mechanical relaxation properties of "mesh-like" and "tree-like" polymer networks were treated. The viscoelastic dynamic network models only with external viscous friction were considered. In [1] it was shown that introducing of the intersegmental or interchain friction forces can have a strong influence on the shape of the relaxation spectra and leads to the drastic change in the time and frequency dependences of relaxation phenomena.

We shall consider the mechanical properties (dynamic modulus and viscosity) and dielectric susceptibility for simple dynamic models of regular polymer networks taking into account the intersegmental and interchain friction effects. The dielectric relaxation was considered for the networks built from macromolecules with dipole moment directed along the end-to-end chain vectors. The effective internal pressure fixing the average volume of the network was introduced preventing the network collapse. It was shown that the relaxation spectra appearing in the dielectric and mechanical phenomena may be quite different. The interchain friction effects lead to the narrowing or cutting-off of the spectra. The short-range (intrachain) and long-range (interchain) relaxation spectra were considered. The qualitative comparison with experiment was made.

This work was carried out with the financial support of the Russian Foundation of Fundamental Investigations, code 96-03-33833a and INTAS Grant 93-2502.

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# REVERSIBLE THERMOTHICKENING OF AQUEOUS SOLUTIONS OF POLYCATIONS FROM NATURAL ORIGIN

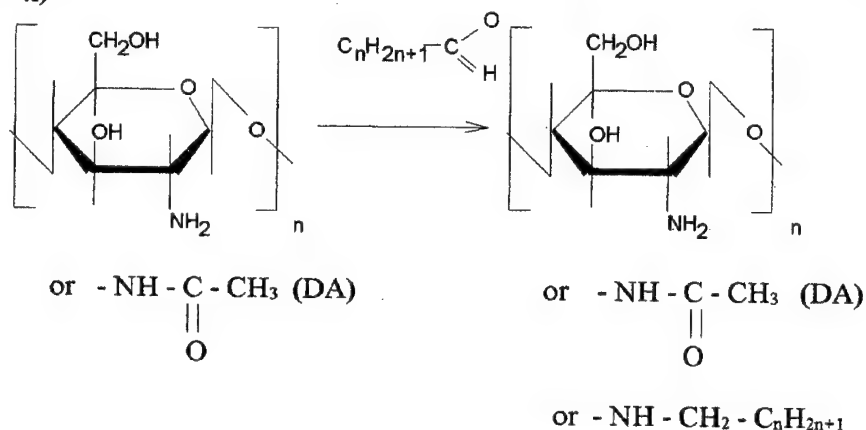
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Chitosan was obtained from chitin by partial deacetylation; chitin is one of the most abundant natural polysaccharides forming crustaceous shells or cell wall of many fungi. After the protonation of amine function chitosan is soluble in acidic conditions ( $\text{pH} < 6$ ) forming a cationic water soluble polymer. The interesting property of chitosan (degree of acetylation  $\text{DA} < 0.5$ ) is that chemical modification can be realized on the N atom at the  $\text{C}_2$  position of the anhydroglucosamine. Alkylation of chitosan was realized with different densities of substituent along the chain and different lengths of alkyl chain (usually  $\text{C}_3$  to  $\text{C}_{12}$ ).



One gets a series of associating polymers whose properties are controlled by the balance between the electrostatic (pH dependent) and the hydrophobic (alkyl chain and temperature dependent) interactions, the external salt playing a role on both interactions.

Few properties related with rheology and light scattering will be discussed in this lecture.

# **THERMAL RELAXATION IN POLED NON-LINEAR OPTICAL SIDECHAIN POLYMERS: INFLUENCE OF ANNEALING**

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The influence of different annealing treatments has been investigated on the stability of the Electro-Optic coefficient in a poled DANS (4-dimethylamino-4'-nitrostilbene) sidechain polymer, which was poled near its  $T_g$ -onset of 140°C. The annealing treatments and the EO relaxation experiments were performed at 120°C. The EO stability can be significantly increased both by an annealing treatment *after* poling and by annealing *before* poling. This latter effect is concluded from the reduction of the EO relaxation rates in consecutive relaxation cycles performed in the same polymer sample - completely depoled and repoled in between the cycles. The effect from the different annealing treatments on the time-dependence of the EO relaxation process is different and is analyzed in terms of Debye-like model with a single, time- dependent Debye relaxation time  $\tau(t)=\tau_i+C \cdot t^B$ . The time-dependence of  $\tau$  and the observed effects from annealing are attributed to the parallel relaxation process of physical ageing.

## Formation and Structural Organisation of Polymer Micelles in Thin Films

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Polystyrene-block-poly(2-vinylpyridine) and polystyrene-block-polyethyleneoxide diblockcopolymers are used to prepare thin micellar films. Three different situations will be discussed:

1. Adsorption of an ultrathin film of a symmetric diblockcopolymer on mica from a nonselective solvent. In this case, an ordered pattern of polystyrene and poly(2-vinylpyridine) surface domains could be observed by scanning force microscopy techniques. Lateral phase separation is explained by unfavourable stretching of the polystyrene chains and the strong adhesion of poly(2-vinylpyridine) on mica favouring a highly stretched conformation of the latter.
2. From a selective solvent for polystyrene (toluene) it has been possible to prepare kinetically stable dry micellar films of varying thickness. The stability of the micelles has been manipulated by ionizing the polar core block either with  $\text{LiAuCl}_4$  or with  $\text{HAuCl}_4$ .
3. Inverse micelles of polystyrene-block-poly(2-vinylpyridine) with a poly(2-vinylpyridine) block which exceeded the polystyrene block in length could be also transformed into metastable micellar films provided sufficiently high molecular weights and ionization of the core block. Due to extensive stretching of the macromolecules, the core diameter is nearly as large as the diameter of the micelles. Relaxation of the metastable structures was shown to yield giant micellar wires with an aspect ratio up to 2000. Transformation of the globular micelles into cylindrical micelles was accompanied by a reduction of the core diameter.

Reduction of the metal salt in the micellar films is employed to prepare small noble metal crystallites of defined size and at defined distances. Thus, glassy polymer materials, which contain optically, magnetically or photochemically active inorganic crystallites of defined concentration size and arrangement can be prepared.

Specific features of the development are:

- a. The size of the microdomains in which the transition metal ions or complexes are concentrated can be rigorously controlled between a few and up to more than 100 nanometers. Also the distance between the domains (inert matrix) can be controlled.
- b. The absolute amount of the transition metal per domain can be varied on purpose.
- c. Molecular mobility and thus crystal growth and ripening kinetics can be controlled by temperature and plastification. Thus, it has been possible to prepare one monocrystal per micelle.
- d. Anisotropic ordering of the crystallites can be achieved.
- e. The chemical structure and properties of the polymer in which the crystallite is embedded can be tailored for optimization of physical properties.

J.P. Spatz, S. Sheiko, M. Möller, *Macromolecules* in press

J. P. Spatz, S. Mößner, M. Möller submitted to *Angew. Chem.*

J. P. Spatz, S. Sheiko, M. Möller, *Adv. Mat.* in press

J. P. Spatz, A. Roescher, M. Möller, *Adv. Mat.* in press

## COPOLYMERS AT INTERFACES

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The adsorption behavior of AB-copolymers at interfaces between two selective solvents are investigated using scaling arguments and Monte Carlo Simulation. Both thermal and asymmetry caused desorption crossovers are predicted on the basis of an Imry-Ma type argument for the dilute surface regime [1, 2, 3]. The simulations are in good agreement with the scaling theory in respect to both the scaling parameter and the asymptotic power law behavior [4, 5]. In the case of an asymmetric interface a multi-critical point appears in the parameter space. Near this critical point fluctuation effects are dominating providing new critical exponents such as the order parameter exponent and the cross-over exponent for single chains. This exponents can be estimated from the simulation data [6]. The work is extended to the semi-dilute surface regime.

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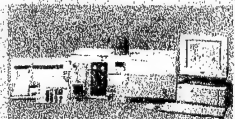


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# CHERRY- AND RASPBERRY-TYPE MICELLES IN BLOCK-COPOLYMER MELTS

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Structure and properties of complex spherical micelles in  $A - B - C$  block copolymer melts is investigated in strong segregation limit. Specific type of  $A - B - C$  block copolymer is considered. It is suggested that monomers of shortest block  $A$  strongly attract one another. The blocks  $B$  and  $C$  ( $N_B \ll N_C$ ) are strongly incompatible. In this polymer system two types of separation are possible: blocks  $B$  and  $C$  tend to segregate because of their incompatibility. Simultaneously the strong aggregation between  $A$  blocks leads to formation small  $A$ -aggregates. As a result the ordered structure of  $B$ -micelles containing in their core small  $A$ -aggregates (multiplets) is formed. If the length of  $B$ -block is much smaller than one of  $C$ -block, the  $B$ -micelles have the spherical form. Properties of  $B$ -micelles are analyzed in the framework of scaling-type theory allowing to calculate the main characteristics of the structure. It was found that the inner structure of  $B$ -micelles significantly depends on the values of surface tensions (between  $A - B$  and  $B - C$  blocks), block lengths and temperature. There are two possible structures of the core of the  $B$ -micelle: i) all  $A$  blocks form one aggregate at the center of the core (cherry-like case): ii)  $A$ -blocks form several aggregates inside the micelle core (raspberry-like case). Depending on the parameters of the polymer system  $A$ -aggregates can have different form.

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## MICELLIZATION IN SOLUTIONS OF CHARGED DIBLOCK COPOLYMER: THEORY AND COMPUTER SIMULATION

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The problem of the micelle formation in the solution of diblock copolymers with one polyelectrolyte and one neutral block in selective solvent is considered. It is shown that the application of scaling arguments of Alexander-de Gennes type to this problem leads to the "open association" picture of the micelle formation. To calculate the critical micelle concentration of the solution in the terms of scaling approach we construct the size distribution function for the micelles. This function in the vicinity of critical micelle concentration (c.m.c.) is rather broad and does not have a pronounced bimodal character. The c.m.c. itself is manifested by the occurrence of the inflection point on the micelles size distribution function. To provide additional support to the theoretical conclusions we present a molecular dynamic simulation of micelles formation in the solution of short polymer chains with attracting end-groups. After long equilibration of the system we obtain normalized distribution function for the micellar aggregation number. Our results are in contradiction with most of experimental observations which correspond to "closed association". Therefore, more experimental and theoretical work is required to achieve an adequate understanding of the structure formation at c.m.c. for block- copolymer solutions.

## HYDROPHOBICALLY MODIFIED POLYELECTROLYTE HYDROGEL/IONIC SURFACTANT COMPLEXES

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To reveal the role of hydrophobic forces in polyelectrolyte gel / ionic surfactant interactions a series of hydrophobically modified (HM) poly(acrylic acid) gels with well-controlled hydrophobicity was prepared by the copolymerization of hydrophilic (acrylic acid) and hydrophobic (n-alkyl acrylate,  $n=8,12,18$ ) monomers.

The interaction of the gels with ionic surfactants, N-cetylpyridinium chloride and sodium dodecylbenzenesulfonate, was studied. Four gel / surfactant combinations were considered: uncharged gel / cationic surfactant, uncharged gel / anionic surfactant, anionic gel / cationic surfactant, and anionic gel / anionic surfactant. The swelling behavior of the gels in the surfactant solutions and the absorption of the surfactant by the gel were examined.

It was shown that the uptake of cationic surfactant results in gel shrinkage, while the uptake of anionic surfactant induces gel swelling. These effects are related with different mechanisms of gel/surfactant interactions. The absorption of cationic surfactant ions proceeds via an ion-exchange reaction with network counterions, while the absorption of anionic surfactant is governed primarily by hydrophobic interactions. Due to conditions of electroneutrality, anionic surfactant penetrates the gel together with corresponding co-ions which enhance the intranetwork osmotic pressure.

The effect of hydrophobic modification of the gel was found to be more pronounced in the interactions with anionic surfactant. In the uncharged gel / anionic surfactant system, binding of surfactant molecules to HM gels starts at a lower surfactant concentration than for the corresponding unmodified gel. In the anionic gel/anionic surfactant system, a significant interaction is observed only for the most hydrophobic gels when hydrophobic interactions overcome the electrostatic repulsion between similarly charged groups.

Thus, hydrophobic modification can improve markedly the gel / surfactant interactions. This can be of pronounced practical interest, in particular, for the purification of raw water from detergents.

**Acknowledgment.** O.E.P. and A.R.K. thank the Russian Foundation for Fundamental Research for financial support.

**POLYMER CHAIN WITH SELECTIVE ADSORPTION OF SEGMENTS:  
MONTE-CARLO SIMULATION OF INTERACTION WITH A PLANE  
IMPENETRABLE SURFACE**

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Great attention has been paid recently to the problem of adsorption of polymer chains with different properties. In this work we cover one more aspect of this problem--interaction of a chain with selective adsorption of segments with a plane impenetrable surface.

A polymer chain with excluded volume and a fraction of segments that attract to the adsorbing surface (whereas other segments undergo only steric repulsion from the surface) is studied by Monte Carlo simulation on a lattice using the bond-fluctuation model of the chain. A short-range adsorption potential is taken: an attracting segment found in the layer nearest to the surface interacts with the surface with the contact energy  $E$ . The critical energy of adsorption and the conformational characteristics of an adsorbed chain (i.e., average number and length of tails, trains, and loops; average height of tails and loops, etc.) are studied for chains of different length  $N=8, 16, 32, 64$  and different fraction of the attracting segments  $\phi=1, 0.5, 0.25, 0.125$ .

We found that in the case of heterogeneous chains (when  $\phi < 1$ ) the adsorption transition occurs at smaller absolute values of the contact energy than in the case of homogeneous chains (i.e., at  $\phi=1$ ) with the same maximum energy of interaction of a chain with the surface at a given value of  $E$ . For heterogeneous chains the dependencies of the average number and length of trains and loops on the contact energy  $E$  also differ from those with  $\phi=1$ . The distributions of segment density near the adsorbing surface are also different for these two cases.

For homogeneous chains ( $\phi=1$ ) the dependencies of the average number and length of tail, train, and loop sections on different parameters of the chain are consistent with the analytical results.

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# THE GYROID PHASE EXISTENCE AND MICROSCOPIC THEORY OF WEAK SUPERCRYSTALLIZATION IN MOLTEN BLOCK COPOLYMERS

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The free energy of the recently observed in molten copolymers gyroid phase (G) is calculated rigorously within the framework of the conventional Leibler weak segregation theory of microphase separation. It is shown that this phase is new stable ordered phase (like well-known body-centered cubic (BCC), hexagonal (HEX) and lamellar (LAM) ones). The corresponding phase diagram is build and reveals the following succession of phase transitions: DIS - BCC - HEX - G - LAM. Thereby, the stability of the phase is due to particular angle dependence of the forth vertex of the corresponding microscopically derived hamiltonian. If the exact form of the dependence is neglected under calculations (as in phenomenological Ohta-Kawasaki theory) the gyroid phase appears (erroneously) to be only metastable. The fact implies that to allow for fluctuation corrections in the gyroid phase the approach of the author and Dobrynin (which is based on a variational principle) should be used rather than conventional Fredrickson-Helfand theory (which also neglects the angle dependence). The corresponding phase diagrams are build for different degrees of polymerization. Possible effects of so-called higher harmonics are discussed as well.

# FLUCTUATION EFFECTS IN THE THEORY OF MICROPHASE SEPARATION IN HETEROPOLYMERS

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We investigate the effect of composition fluctuations on the microphase separation transition in symmetric  $A-B$  multiblock copolymers, of which chains consist of a stochastic sequence of flexible segments. The analysis is facilitated by reducing the multiblock copolymer Hamiltonian to a form previously studied by Brazovskii. Within the framework of Hartree-Fock approximation we obtain the following principal results: (i) A symmetric polyblock copolymer is predicted to undergo a first order phase transition at a larger value of  $\chi N$  than the third order transition in mean field theory. The Flory interaction parameter is denoted  $\chi$  and  $N$  is the number of statistical segments of  $A$  and  $B$  blocks. (ii) The lamellar microphase is favourable at phase transition from a disordered phase to the ordered one. The transition is predicted to follow the pattern: *disordered*  $\rightarrow$  *disordered+lamellar*  $\rightarrow$  *lamellar* phases. The locations of the disordered  $\rightarrow$  two-phases transition and two-phases  $\rightarrow$  lamellar one are at  $(\chi N)_1 = 2 + 1.86N^{-1/4}$  and  $(\chi N)_2 = 2 + 2.76N^{-1/4}$  respectively. (iii) The mean field theory is applicable in the limit of  $N \gg 1$ , which is the case for actual polymers.

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# THEORY OF DEPOLARIZED SCATTERING OF POLYMER BLEND NEAR CRITICAL POINT

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The theory of depolarised scattering of two component homopolymer blend near critical point is presented. We found that depolarized scattering can be explained by double scattering process. Expression for depolarized intensity of light scattering contain singular and nonsingular parts. Second part becomes significant for rather small molecular weight and far enough from the critical point.

We calculate dependencies of the intensity of light scattering as a function of temperature and investigate dependence on molecular weight. We also investigate dynamic dependencies of intensity of depolarized scattering. We predict a non-exponential decay for this intensity. All results have a good agreement with experimental data. We also explain the difference between intensity of PDMS/PEMS and other polymer blends (PS/PB and PS/PI) by considering the non-singular part in main equation.

The presented scheme of calculations can be used to investigate depolarised scattering from diblock copolymer melts.



# SYNTHESIS OF THE FULL PHASE DIAGRAM FOR POLY - $\gamma$ - BENZYL - L - GLUTAMATE / DIMETHYLFORMAMIDE SYSTEM ON THE BASE OF DIFFERENT EXPERIMENTAL DATA

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On the base of critical review of data obtained by different authors a new phase diagram for PBG/DMF system was constructed (see Fig.) at quantitative level. This diagram coincides qualitatively very closely with that proposed previously by Papkov for rigid polymer/solvent systems with possible crystallosolvate (CS) formation taking into account. The existence of CS phase explained many properties of systems and specific features of phase diagrams at all concentrations. Some new concepts such as limited LC-phase, different types of CS-phase defects etc. are introduced. Quantitative molar relations for PBG and solvent are calculated in different regions of phase diagram.

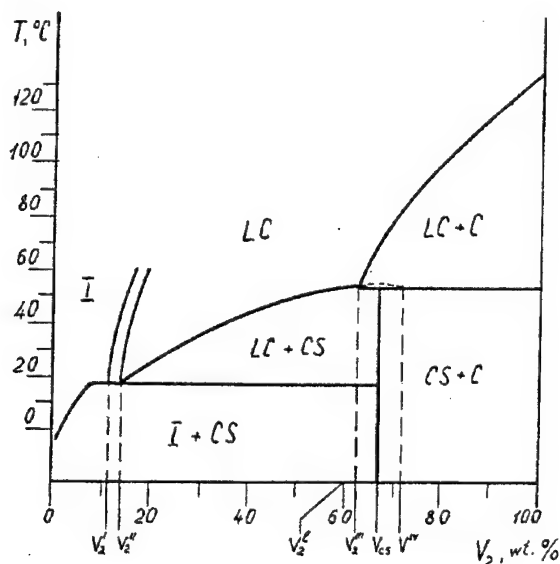


Figure. I - isotropic phase; LC - liquid crystalline phase; CS - crystallosolvate phase; C - crystalline phase;  $V_2'$  and  $V_2''$  - the first and the second critical concentrations, corresp.;  $V_2^1$  - concentration of "limited" liquid crystalline phase;  $V_2'''$  - the boundary of congruent and incongruent melting of CS phase;  $V_{cs}$  - concentration of 100% CS phase

## AN AUTOWAVE REGIME IN REACTING POLYMER BLEND.

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A quasi-autowave regime was found for the set of reactive-diffusion equations describing the evolution of compatible polymer blend.

A model system of two adjoined homopolymer films A and B was considered. At  $t=0$  the interdiffusion starts accompanied by the reaction in which A units transform (with rate constant  $\gamma$ ) into B-ones if contact with B-units. The reaction was believed to be kinetically controlled. Macroscopic reactive-diffusion equations were written for two collective variables  $\phi$  and  $\rho$ :

$$\begin{aligned}\frac{\partial \phi}{\partial t} &= \bar{\nabla} \left( D_{\phi\phi} \bar{\nabla} \frac{\phi}{T} \right) + \bar{\nabla} \left( D_{\phi\rho} \bar{\nabla} \frac{\rho}{T} \right) \\ \frac{\partial \rho}{\partial t} &= \bar{\nabla} \left( D_{\rho\phi} \bar{\nabla} \frac{\phi}{T} \right) + \bar{\nabla} \left( D_{\rho\rho} \bar{\nabla} \frac{\rho}{T} \right) - \gamma \rho (1 - \rho),\end{aligned}\quad (*)$$

where  $D_{ij}(\rho, \phi)$  - matrix of interdiffusion coefficients,  $\phi(r, t)$  and  $\rho(r, t)$  - volume fractions of reacting chains (initially homopolymer A) and reacting units (A-type) respectively.

It was shown analytically that for large  $t$  the profile of  $\rho$  satisfies the Fischer-Kolmogorov-Petrovskii-Piskunov (FKPP) equation, irrespective to initial conditions. It means that the front of reacting units moves through A-film with constant velocity and permanent shape.

An interesting long-lived regime was found for the profile of  $\phi$ . At the early stage of the reaction under certain conditions a small part of B-chains may be sucked in the reacting chains' layer. As a result the profile of  $\phi$  becomes non-monotone. Then sucked chains move with the front of the reaction (the profile of  $\rho$ ) and accelerate it considerably. Such type of chain transfer proceeds much faster than the ordinary interdiffusion of other catalytic chains. This regime was observed in the numerical solution of the equations (\*). Finally, if A-film is sufficiently thick the profile of  $\phi$  becomes spatially monotone again while the profile of  $\rho$  meets the FKPP equation.

The conditions for appearance of this non-trivial diffusion regime were investigated both numerically and analytically. The proper values of system parameters were determined, such as chains A and B lengths' ratio, Flory-Huggins parameter, the thickness of initial boundary between the films. It was shown that the lifetime of the non-monotone region on the profile of  $\phi$  may be found as the retention time of diffusion for the particle localized in a potential well of certain shape.

For numerical calculations the authors used the software kindly given by Dr. A.G.Makeev. Financial support from Russian Fund for Basic Researches (Grant 95-03-09584a) is gratefully acknowledged.

## SPINODAL DECOMPOSITION IN REACTING POLYMER BLEND.

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Macromolecular reactions in incompatible polymer blends provide a promising way to obtain new composites that can be more compatible and durable. At present there is no proper theory of such processes. We suggest the description of competition between phase separation and block-copolymer formation in polymer blend.

Consider an initially homogeneous blend of homopolymers A and B. After a temperature jump initiating the phase separation, the diblock-copolymer formation through end-chain coupling proceeds simultaneously with spinodal decomposition. The reaction is supposed to be kinetically controlled. We derived the reactive-diffusion equations for the structural factors matrix valid at the linear stage of spinodal decomposition. The  $\mathbf{k}$ -dependent kinetic coefficients ( $\mathbf{k}$  is the wave vector) were calculated using the fast-mode interdiffusion theory.

The set of equations was examined numerically for various values of the parameters (diffusion coefficients, reaction rate constants, chain lengths of homopolymers, the Flory-Huggins parameter). In particular we examined the correlation function between fluctuations of A-units  $S_{AA}(\mathbf{k})$  that can be measured in scattering experiments. The reaction was shown to slow down significantly the segregation process. The conditions were analyzed for which the reaction suppresses phase separation during the linear stage of spinodal decomposition.

The results obtained are in qualitative agreement with experimental data related to spinodal decomposition of blends containing diblock-copolymer and to reactive compatibilization of polymer blends.

Financial support from Russian Fund for Basic Researches (Grant 95-03-09584a) is gratefully acknowledged.

## MODEL HYDROPHOBICALLY END-CAPPED POLY (ETHYLENE OXIDE)

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We have previously shown that the phase diagrams in water of model hydrophobically end-capped poly(ethylene oxide) with paraffinic extremities of 12 carbon atoms can exhibit several domains :

- i) monophasic domains corresponding to an homogeneous dispersed solution, a micellar solution and a micellar cubic phase
- ii) biphasic domains corresponding to a demixing between a lamellar and a cubic phase at high concentration and a demixing between a dispersed solution and a micellar solution at lower concentrations.

There is an evolution of the diagrams according to the molecular weight of the PEO chain, the cubic phase occurring only if  $M_w < 6000$ .

The present work deals with the behaviour of polymers end-capped with C18 groups with the influence on the phase diagram and on the structural parameters of  $\tau$ , the degree of substitution. Indeed for a partial substitution, the system contains a mixture of bi, mono and unfunctionalized macromolecules. In most previous works, rheological studies of the aqueous solution of this type of associative polymers were performed on such mixtures and besides the degree of functionality was never clearly indicated.

For  $M_w=20\ 000$  the phase diagram has a region of phase separation at low concentration. The minimum temperature of the demixing curve increases when  $\tau$  decreases. At room temperature the completely modified polymer phase separates for  $C_1 < C < 5\% C_1$  being very close to the concentration where fluorescence measurements show the formation of hydrophobic microdomains. The demixing line between the homogeneous phase and the lamellar phase corresponding to the chain crystallisation doesn't depend on  $\tau$ .

The structure of the homogeneous phase which is characterised by the appearance of one or two peaks in the neutron scattering experiments is enhanced when  $\tau$  increases. The distance between the hydrophobic microdomains decreases when  $\tau$  increases. Some results obtained by labelling the end groups by deuteration allow us to define the size and shape of the microdomains.

## AGGREGATION OF BLOCK COPOLYMERS WITH CONJUGATED SEQUENCES.

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In order to make soluble unsubstituted conjugated polymers we have synthesized block copolymers including a soluble sequence ( polystyrene) and a conjugated insoluble sequence (polyparaphenylene , polythiophene). The synthesis of these PS-b-PPP and PS-b-PT copolymers will be described. S.E.C. analysis , Light and Neutron Scattering studies show that they are organized, in THF or solution and in the solid state, in micellar aggregates with a well defined conjugated cores. The size of these cores (60 -250) and the high degree of aggregation are measured and correlated to the molecular weight of sequences. X.R. measurements indicate a crystallinity in the PPP cores.

We have also synthesized a set of Polystyrene-poly 3 hexylthiophene (PS-P3HT) block copolymers. In this case the conjugated sequence is soluble . Neutron scattering by THF solutions shows that the P3HT sequence behavior corresponds to a linear chain with an excluded volume effect. The local structure of the skeleton is described by a model of persistence length chain ( $L_p \sim 33$  , corresponding to 8-9 monomers units). Doping induces an aggregation of P3HT sequence . In the solid state a comparative study by X.R. of undoped PS / P3HT blends and PS-P3HT copolymers shows neat interface in both cases ( The Porod 's law  $I \sim 1/q^3$  is followed with linear collimator). The Bragg's peak corresponding to the 16 Å distance between P3HT chains is nevertheless well defined only in copolymers spectra. This means that a separation into pure phases (PS and P3HT) occurs with copolymers while this is not true for blends.

The formation of conjugated nanodomains dispersed in an isolating matrix induce a considerable improvement of photo and electroluminescent properties of these conjugated sequences in comparison with the pure homopolymers.(1-2)

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# FILMS WITH HONEYCOMB MORPHOLOGY FROM FUNCTIONALIZED POLYSTYRENES OR BLOCK- COPOLYMERS. IMPORTANCE OF THE CHAIN AGGREGATION IN THIS PROCESS.

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We have discovered that carbon disulfide solutions of polystyrene-polyparaphenylene (PSt-PPP) block copolymers quickly evaporated in an atmosphere containing water vapor produce films with an exceptional honeycomb morphology, made of spherical pores (size: 0.5 to 10 microns) arranged upon an hexagonal network (1). Pores of the upper layer are open forming regular hexagonal arrangements of perfectly identical holes. Photos taken with optical and scanning electronic microscope or with A.F.M are presented. This same result has been obtained with a polystyrene-polythiophene (PSt-PT) block copolymer. It will be remarked that PPP and PT homopolymers are unsoluble. A newly synthesized polystyrene- poly 3 hexyl thiophene (PSt-P3HT) block copolymers, with both soluble sequences, lead also to a similar morphology in their (aggregated) doped state but not in the (non-aggregated) undoped state (2). The common characteristic of these copolymers, which are able to form a regular honeycomb morphology, is the strong aggregation of the conjugated sequences inducing a starlike organization of the polystyrene part.

It is remarkable that in the same experimental conditions linear polystyrenes does not give such regular morphology.

The importance of the starlike aggregation was highlighted by using polystyrenes bearing at one end a polar group which are able to associate, in non polar solvent such as CS<sub>2</sub>. Similar morphologies were indeed obtained with solutions of polystyrenes ( $M_w = 5000$  and  $15000$ ) capped at one end by either the lithium salt of sulfonic acid (I), or by a sodium carboxylate (II), or by a sodium alccoolate (III).

The proposed mechanism of formation is the following : The quick evaporation of the solution induces a cooling and the condensation of a water droplets layer with an hexagonal arrangement at the surface. This layer acts as a matrix for the pore formation in the film. It was observed from parallel experiments that the starlike organization of polymers decreases the polymer solution /water interfacial tension and make more easy the formation of a polymer film at this interface. This polymer film would prevent the droplet coalescence and is expected to regulate their size .These both effects are less important with linear polystyrenes explaining thus their irregular morphology.

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# ASSOCIATIVE STRUCTURE AND DYNAMICS OF HYDROPHOBICALLY END-CAPPED POLY(ETHYLENE OXIDE) AQUEOUS SOLUTIONS.

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The hydrophobically end-capped poly(ethylene oxide) samples with different PEO chain length ( $M=10000$  and  $M=20000$ ) [J.Francois, Progress Org. Coat., 1994, 24, 67] were investigated in water by the following methods: light-scattering, velocity sedimentation, translational diffusion and viscometry.

The data characterising molecular and thermodynamic parameters of the system were obtained by a standard procedure with a Sofica photogoniometer and treated by the Debye method. These data indicate the associative processes in water that are more pronounced for the sample with a shorter PEO chain. It is shown that even at infinite dilution the solution contains associates consisting of 5 macromolecules for the sample with  $M=10000$  and 3 macromolecules for the one with  $M=20000$ .

The data obtained to process indicatresses of anisotropy and isotropy scattered components of vertical polarized incident light and treated in the frame of the statistical theory [R.S.Stein and P.R. Wilson, Appl. Phys., 1962, 33, 1914] showed for the sample with  $M=10000$  the existence of associative supermolecular structure. The associate dimensions decrease as the concentration increases. The associates are optically anisotropic. The reduced anisotropy of the system decreases as the concentration increases. The mutual scattering elements orientation in the macromolecular ensemble was high ( $\langle \cos\theta_{ij} \rangle = 0.8$ ) and constant in the investigated concentration range.

The sedimentation and diffusion analysis pointed out the existence of associates along with the individual macromolecules in dilute solutions. However, the associates are destroyed under the action of hydrodynamic field of the ultracentrifuge. The values of the associate molecular weights obtained by this method are in good correlation with the values obtained by the light-scattering.

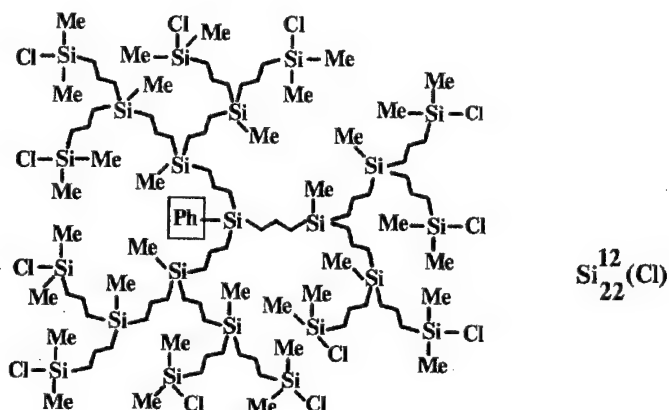
The comparison of structural peculiarities for the hydrophobically end-capped PEO in water observed under the static conditions and under the action of hydrodynamic field is carried out.

# BLOCK-COPOLYMERS OF NEW TYPE BASED ON MULTYFUNCTIONAL DENDRITIC BRANCHING CENTERS

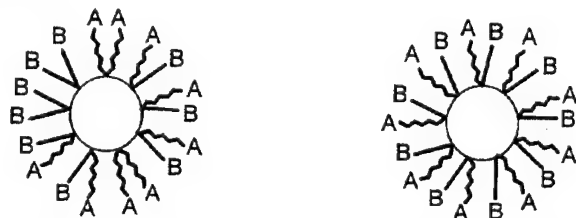
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It is well known that the architecture of blockcopolymers determines block's possibility of aggregation and phase separation. In recent years the appearance of dendrimers (or cascade polymers) with dual nature particle - macromolecule, allow us to elaborate schemes of synthesis of blockcopolymers with unusual architecture. In suggested schemes various combinations of blocks with different chemical nature and multifunctional branching center of dendritic structure were used. The synthesized carbosilane dendrimer that has been employed as branching center is presented below.



Well-characterized monofunctional blocks with different nature can be consecutive grafted to dendrimeric branched core to give series of block-copolymers. The different structures of functional groups on outer surface of dendrimer allows to form regular or random block-copolymers:



Obtained block-copolymers can be suggested as the objects to study specificity of microphase separation and self-assembling processes.

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## THE EFFECT OF THE STRUCTURE OF NONIONIC BLOCK COPOLYMERS ON THEIR CLOUD POINTS

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Cloud point has been widely used to characterize surfactants. In spite of the extensive use of cloud point, its relationship with the structure of the surfactant has not been systematically studied. An effort was made to study the relationship between structure of certain polyoxyalkylene block copolymers and their cloud points. Following block copolymers were synthesized by the anionic living polymerization of epoxides:

(EO)(PO)(EO)

(EO)(BO)(EO)

(PO)(EO)(PO)

(BO)(EO)(BO)

where EO= ethylene oxide (hydrophilic) unit, PO= propylene oxide (hydrophobic) unit, and BO= butylene oxide (hydrophobic) unit. The cloud points for these poloxamers as 10% water solution were measured [1]. Similar to earlier studies [2], we have observed a correlation between cloud point and weight percentage of ethylene oxide. We observed that the dependence of cloud point on the percentage of ethylene oxide is more pronounced with low molecular weight polypropylene oxide block. The cloud point logarithmically decreases with increasing number of propylene oxide units.

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A SCALING LAW FOR THE EFFECT OF HARD-SEGMENT  
LENGTH ON THE EQUILIBRIUM LAMELLAR MORPHOLOGY  
IN POLYCAPROLACTONE-POLYPROPYLENE GLYCOL-  
POLYCAPROLACTONE (PCL/PPG/PCL) TRIBLOCK  
COPOLYMERS

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The spherulitic growth rate of PCL/PPG/PCL triblock copolymer with constant length of PPG ( molecular weight= 4,000) and various length of PCL blocks ( molecular weights= 2,500 to 35,000) was measured with polarizing microscopy. Equilibrium meltig points of copolymers by Hoffman-Weeks equation and surface fold energy of copolymer lamellae by Hoffman nucleation theory enabled the determination the equilibrium length ( $L_c$ ) of fully extended lamellar morphology in copolymers. It is found that the number of chain folding in lamellae increases with length or weight content of PCL blocks, and  $L_c$  can be scaled as a power function of molecular weight of PCL blocks ( $\bar{M}_n$ ):

$L_c \approx \bar{M}_n^{0.78 \pm 0.07}$ . The exponent with respect to  $\bar{M}_n$  deviates from the unity, as predicted from the theories by DiMarzio et al. and by Whitemore and Noolandi. It is also theoretically shown with the free energy of microdomain that, such a deviation is due to the incorporation of localization energy at the joints connecting soft and crystallizable blocks, which is totally negligible in amorphous-amorphous block copolymers.

Keywords: Poly( $\epsilon$ -caprolactone) copolymers; spherulite growth; nucleation; segmental diffusion; phase segregation.

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## **SORPTION CHARACTERISTICS AND DOMAIN STRUCTURE OF POLYBLOCK POLYORGANO-POLYSILOXANES**

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Membranes for gas separation prepared from polyblock polyorgano-polysiloxane copolymers ( e.g. polyarylene- and polycarbonatesiloxane) show high gas permeability and selectivity. The principal drawback of these compounds limiting their application is the variation with time of the sorption and strength characteristics. These properties are known to depend essentially on the microheterogeneous structure of this material and therefore the stability of the service characteristics of the polymers may be ensured by stabilization of their structure. The present study using inverse gas chromatography is concerned with sorption characteristics and domain structure of the block copolymers. Our data show that the structure of the polymer can be stabilized by introducing into the bulk of polymer small amounts (1-2 % wt) of modifiers (phthalates, certain terpenes, and squalane). The sorption properties and strength of the modified block copolymer remained unchanged for a long time as showed our measurements performed within 5 years. The changes in the corresponding unmodified block copolymers appeared already within a month. The electron microphotography has demonstrated that the stabilization is achieved due to adsorption of the modifying substance on the surface of the domains formed by the rigid polyarylene blocks. Gas chromatographic studies and small angle X-ray scattering has also revealed that the additive provides more complete phase separation in the polymer and reduces the proportion of the interphase layers in the bulk of the polymer. The resulting gas permeability and selectivity of the membranes is close to those of the polydimethylsiloxanes. The gas permeability of the thin block copolymer films towards some hydrocarbons was quantitatively estimated as a function of the polymer composition and of the presence of the modifying additive. The presence of the additives was shown to increase the stability of the membranes to aggressive gases (e.g., to sulfur dioxide).

**SORPTION PROPERTIES AND STRUCTURE OF  
POLYFLUORINATED COPOLYMERS CONTAINING  
THERMODYNAMICALLY INCOMPATIBLE COMPONENTS**

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Copolymers of ethylene with perfluoroethers owing to their high chemical and thermal stability attract attention as a perspective material for selectively permeable membranes designed for service in aggressive media at elevated temperatures. We have prepared six copolymers of hydrocarbon and perfluorinated monomers with general structure  $[(CH_2-CH_2)_x - CF(O - R_f)CF_2]_n$  and have investigated their sorption and diffusion characteristics. Some perfluoropolymers were investigated for comparison. The sorption characteristics of polymers were studied by means of inverse gas chromatography as a function of chemical structure features, e. g. relative length of hydrocarbon and perfluorinated chain segments, length of side branches and rigidity of the latter, and the presence of functional groups. The data obtained are used for evaluation of thermodynamic characteristics ( $\Omega_1^\infty, \Delta H_s, \Delta H_1^{E\infty}, \Delta S_1^{E\infty}, \chi_{1,2},$ ) of polymer-sorbate systems for a series of hydrocarbon and perfluorinated compounds. We have also estimated the solubility parameters and solubility factors of the sorbates in the polymers under study. These data are important for predicting the application performance of the membranes. The diffusion properties of the copolymers indicate that their free volume is considerably larger than that of perfluorinated polymers. This feature is due to the thermodynamic incompatibility of the copolymer components and to the presence of bulky side branches. The specific characteristics of thin films prepared from the copolymers were studied by means of small angle X-ray scattering and by electron microscopy. Microheterogeneity of the polymer structure was demonstrated that occurs due to formation of clusters enriched with hydrocarbon component. Functional groups in the side chains (e. g. sulfofluoride groups) lead to formation of a regular physical network due to association of the lateral branches.

## MACROMOLECULES OF MULTIBLOCK COPOLYMERS IN SOLUTION

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The problem which is of our main interest here is a comparison between structures of solution of multiblock copolymer - polysiloxanecarbonateurethane - in three solvents with a widely different thermodynamic quality:

1. Common solvent with a nearly equal thermodynamic quality in relation to each of the blockcopolymer components - THF,
2. Selective solvent (benzene) which is nonsolvent for carbonate block;
3. Common solvent (dioxane) characterized by quite different thermodynamic quality in relation to each of the components. We named this solvent as semiselective. The results of light scattering measurements and viscometry are presented in Tables 1 and 2.

Table 1. The second virial coefficient-  
of blocks

Solvent	Siloxane $A_2 \cdot 10^4$	Carbonate $A_2 \cdot 10^{-4}$		Solvent	$M_w \cdot 10^{-3}$	Z	$[\eta]$
THF	12	26		THF	40	1.1	0.460
Benzene	6	<0		Benzene	2000	$\approx 1$	0.285
Dioxane	2	22		Dioxane	200	3.6	0.470

Table 2 Characteristics of copolymer

In summary it may be said that particles of copolymer in semiselective solvent consist of more than one macromolecule at contrast to the molecular solution. But at the same time these particles have no core as it is in selective solvent at formation micelles. For these reasons the size of such particle is much more than it is both in genuin and in selective solvents. In addition the structure of these particles is kept invariant to dilution of the solution but too responsive to temperature and initial concentration on dissolving of copolymer.

This reseach was supported by the Rusian Science Foundation  
(grant 95- 03- 08558a ).

## Dielectric spectroscopy and phase structure in compositions of Polyisoprene-Oligoesteracrylates.

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Relaxation properties of compositions of Polyisoprene (PI) with oligoestersacrylates (OEA) have been studied by dielectric spectroscopy over frequency range  $1\text{-}10^5$  Hz at the temperature from 150 K to 420 K. The oligomer contents was varied from 0 to 100 % weight in these compositions.

The consideration of relaxation properties and phase structure were started from the homocomponents (PI,OEA).

Dielectric transition in PI due to segmental motion (the region of  $\alpha$ - process) was observed near 216 K ( $f=10^3$  Hz).

There is the only region of dielectric losses at 204 K ( $f=10^3$ Hz) in the gomooligomer. It was shown by the dielectric investigations this region was connected with the motion of the molecules OEA as a whole .

Relaxation properties of the compositions and hence their phase structure strongly depend on the components ratio.

All the compositions which have OEA to 3% exhibit only one the dielectric absorption process with the relaxation times equal to that in the homopolimer PI ( $\alpha$ -transition in the phase of PI).

For the compositions containing OEA from 5 to 35% three regions of the dielectric losses were found. The relaxation times of two of them coincide with that in homocomponents. Therefore these two dielectric processes were interpreted as glass transitions in the PI phase and OEA phase. The relaxation time of the third process at the highest temperatures depends on the oligomer contents: the OEA contents is greater the relaxation time is longer. It is shown that the third region of dielectric absorption is related to the mobility of OEA molecules surrounded by PI macromolecules. Unusual fact has been observed: the relaxation times of this transition are longer than that for OEA molecules in bulk. It is connected with the restrictions of OEA molecule motion due to the association and formation of microphase of OEA particles.

In compositions with contents of OEA 35% and more the third relaxation process has different properties. The relaxation times in this region decrease and approach to that in the homooligomer when the contents of OEA increases. In this case the phase structure of compositions can be considered as a OEA phase with the included PI molecules.

The work was supported by Fundamental Research Foundation of Russia  
( Grant 96-03-33850a).

# **POLYDIMETHYLSILOXANE TELECHELIC IONOMERS: REOLOGY OF THE BULK AND IONOMER SOLUTIONS**

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A series of telechelic siloxane Li-, Zn- and Ni-containing ionomers was prepared by partial or complete neutralisation of carboxyl- containing polydimethylsiloxane telechelics with various polymer chain length.

Viscosity curves were obtained for some of siloxane ionomers synthesised. A presence of ionic groups in such systems leads to a substantial increasing of viscosity in comparison with initial acid polydimethylsiloxanes. Investigation of temperature dependences of the viscosities of these siloxane ionomers showed that the activation energy for viscous flow depended on the nature of metal ion.

Viscosity-concentration curves for Li- and Zn-containing siloxane ionomers obtained in two types of solvents: apolar (m-xylene) and mixture solvent (m-xylene and ethanol) demonstrated essentially different characters.

Some polymer solutions exhibited a shear-thickening behaviour.

## **Acknowledgement**

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**POLYMORPHISM OF THE ASSOCIATES OF DIPHYLIC  
IONS IN AQUEOUS SOLUTIONS OF THE CATIONIC  
POLYELECTROLYTES.  
THE RELATIONSHIP OF THEIR STRUCTURE WITH  
BIOLOGICAL AND PHYSIOLOGICAL ACTIVITY.**

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The methods of spectral shift of the dye (methyl orange), nuclear magnetic relaxation and static light scattering have been used to estimate the role of water in the formation of the microenvironment and structure of polyelectrolyte complexes (PEC) based on the copolymer of N-vinylpyrrolidone and iodine ethylate of N,N-diethylaminoethyl methacrylate with sodium dodecyl sulfate (SDS).

It was established that at the molar ratios ( $\gamma$ ) of SDS to the cationic units of copolymer equal to 0.5 and 1.0, complexes greatly differ in the degree of hydrophobicity of microenvironment and the quantity of bound water. Moreover, with respect to topology PEC are intramolecular pseudomicellar clusters of SDS molecules electrostatically bonded to polycation.

For nonstoichiometric PEC at  $\gamma$  value of 4.0 the formation of discrete structure is characterized by high hydrophobicity of the polymeric domains and high capacity for binding water molecules which are strongly polarized. It is assumed that at  $\gamma=4.0$  the PEC structure is formed according to the type of pseudolamellar clusters of SDS molecules stabilized by hydrophobic interaction with SDS molecules electrostatically bonded to polycation.

This marked change in the microenvironment of PEC at the  $\gamma$  value increasing from 0.5 to 4.0 is accompanied by the change of PEC molecular-conformational parameters (dimensions and MM).

The differences in the structure and physico-chemical properties of PEC at different  $\gamma$  values are reflected on the biochemical level (inhibition and activation of tryptic hydrolysis), on the membrane level (different character of the PEC effect on the permeability of lipid bilayers), and on the level of living organism (oppression and activation of the animal growth processes).



## MOLECULAR CHARACTERISTICS OF IONOMER AND IONOMER - SURFACTANT COMPLEXES IN M-XYLENE

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Hydrodynamical, dynamo- (flow birefringence) and electrooptical (Kerr effect) properties of sulfonated polystyrene ionomers (1,35 molar percent of  $\text{SO}_3\text{Na}$  salt groups) (SPNa), sodium bis-(2-ethylhexyl) sulfosuccinate (aerosol OT or AOT) molecules and complexes of SPNa+AOT ( $[\text{SPNa}]/[\text{AOT}] = 2,5$  in monomers moles) as well as SPNa+AOT+ $\text{H}_2\text{O}$  ( $[\text{AOT}]/[\text{H}_2\text{O}] = 1/5$  in moles) in low-polarity organic solvent m-xylene were studied. Dependences of sedimentation  $S$ , diffusion  $D$  coefficients, reduced viscosity  $\eta$ , electric birefringence (EB) and relaxation times (rotational diffusion coefficient) on solutions concentration  $c$  were investigated. A nonlinear changes of  $\eta$ ,  $S$  and  $D$  values as well as a big value of EB and nonexponential rise and decay of EB confirms the existing of intermolecular aggregation in solutions of SPNa ( $c > 0,2$  g/dl), AOT ( $c > 0,2$  g/dl), SPNa+AOT and SPNa+AOT+ $\text{H}_2\text{O}$  ( $c > 0,5$  g/dl). The increasing of molecular weight  $M$  of SPNa molecular aggregates with solution concentration  $c$  in according to  $M \sim c^{0.5}$  was established. From translation diffusion, sedimentation and viscosity data in dilute solutions of SPNa ( $c < 0,2$  g/dl) the decreasing of single coils dimensions as compared with that of polystyrene (PS) coils with the same degree of polymerization in m-xylene was founded. That is caused by the multiplex intramolecular interaction between ionomer salt groups. In the presence of AOT molecules or reversing micelles of AOT the reduced viscosity (for  $c < 0,47$  g/dl) and diffusion coefficient  $D$  (for  $c < 0,1$  g/dl) in SPNa+AOT and SPNa+AOT+ $\text{H}_2\text{O}$  solutions are near to  $\eta$  and  $D$  of PS. Dimensions of single coils of investigated polycomplexes correlates with that of PS with the same degree of polymerization in m-xylene. Analysis of translation diffusion, sedimentation and EB data shows that about 50% of AOT molecules or reversing micelles of AOT are associated with SPNa salt groups and forms stability ionomer-surfactant complexes in nonpolar solvent.

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**A STUDY OF COMPLEX FORMATION  
BETWEEN HYDROXYPROPYL CELLULOSE AND  
HEXADECYLTRIMETHYLAMMONIUM BROMIDE  
BY MEASUREMENTS OF SOLUTION VISCOSITY AND  
DIFFUSION COEFFICIENT**

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The formation of complexes between hydroxypropyl cellulose (HPC) and hexadecyltrimethylammonium bromide (HTAB) was identified by measurements of solution viscosity and the complex hydrodynamic radius which was obtained by dynamic light scattering technique. HPC is a nonionic polymer whereas HTAB is a cationic surfactant. The essential interaction between the nonionic polymer and the cationic surfactant is hydrophobic, even though other interaction mechanisms are present. We found that the maximum size of the complex occurs when HPC concentration is about 0.02 percent by weight. This critical HPC concentration is independent of the HTAB/HPC ratio which was varied between 0.005 to 0.04. The corresponding critical value of the HTAB/HPC ratio is about 1.25 and seems to be independent of the HPC concentration which was varied between 0.005 to 0.04 % wt. The adhering of surfactant micelles on the hydrophobic part of HPC changes the nonionic polymer to a polyelectrolyte. This was shown by the dependence of the complex size on the added salt content; the presence of salt or counterions acts to shield the electrostatic interaction and therefore promotes contraction. We also investigated the correlation between viscometric functions and the diffusivity and compared the results with the correlations of other polyelectrolytes and neutral polymers.

## INTERACTION BETWEEN POLYACRILIC ACID AND DIFFERENT NONIONOGENIC POLYMERS.

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The polymer mixing is an effective method of the purposeful property regulation of polymer materials. Besides important practical application of polymer blends the studies of their properties give new information of polymer mixture structure. The interactions between a polyelectrolyte and a nonionogenic polymer in several cases lead to interpolymer complex formation. This assumption is confirmed by results of viscosity measurements and vapour solvent sorption of polymer blend and pH-measurements of the mixtures.

In our studies the interaction between aqueous solutions of polyacrylic acid and nonionogenic polymers (polyvinyl alcohol, hydroxyethylcellulose and methylcellulose) were studied by such measurements. Polymer concentration, mixture composition were varied. The measurements were carried out at the constant temperature.

The polymer compatibility in the mixture is studied in the first place. If the polymers are compatible it is important to study the interaction parameter. The negative values of interaction parameters of mixture components would be a sufficient condition of mixture compatibility. The dependences of polymer-polymer interaction parameters on the mixture composition was studied by the method of vapour solvent sorption. Experimental data show the presence of a minimum on the corresponding curves. For all systems values of the interaction parameter are calculated and all of them are negative in complex formation region. The result of this studies is in good agreement with data for the same mixture composition obtained from viscosity studies, the concentration influence being taken into account.

The deviation of the experimentally determined relative viscosity of a polymer mixture, from the calculated value could be used as measure of the interpolymer interactions. In our work, where one of the two polymers, PAA, is a polyelectrolyte and consequently its reduced viscosity increases considerably with decrease of its concentration (polyelectrolyte effect), in order to calculate the above mentioned ideal curve we have used the experimentally determined relative viscosity of PAA at the different concentrations at which it exists in the polymer mixtures of different compositions.

Viscometric tests for all systems showed the non-additive behaviour of the dependences of viscosity on mixtures composition. The marked positive (systems PAA-PVA, PAA-HEC) and positive and negative (PAA-MC) deviations of the experimental curve from the calculated one demonstrated interaction between the two polymers in the mixture. The formation of interpolymer complexes was additionally proved by pH-measurements. It was shown that complexes are formed due to the hydrogen bonding between nondissociated groups of polyacrylic acid and proton acceptor groups of the other component.

The results show that all the components of the mixtures are compatible due to their preferential interaction in the mixture.

### Acknowledgements.

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## WATER WITHIN GELS BASED ON POLY-N-VINYLCAPROLACTAME (PVCI)

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The elucidation of a specific role for water in stability of proteins, functioning of enzymes, water selective transfer through reverse-osmosis and pervaporation membranes based on aromatic polyamides, complexation of polyvinylpyrrolidone, and so on requires an establishment of structural transformation with water associates being in an environment of amide and nonpolar groups.

Important information concerning the physico-chemical properties of water was found when studying phase transitions (melting and evaporation) of water within gels based on crosslinked polymer containing amide groups namely *PVCI* by *DSC* and thermogravimetry methods. The value of melting heat ( $\Delta H_{mt}$ ) for an "ice within the *PVCI* net" is lower than  $\Delta H_{mt}$  for an ice in bulk water (334 Joule/g). With decreasing the number of molecules on repeat unit ( $N$ ) from 15 to 5 it reduces considerably from 180 to 54 Joule/g, respectively indicating on essential rupture in structural water organization of ice crystals.

In addition to, it was displayed an appearance of two peaks (low temperature and high temperature) on thermogrammes of water evaporation from *PVCI* gel. The features of water evaporation from water within *PVCI* net are low temperature of evaporation start (70°C) and high one of evaporation end (167°C) in comparison with pure water (97°C and 147°C) under the same heat conditions. The value of  $\Delta H_{ev}$ , calculated from all area of thermogrammes at various  $N$  being 1880 Joule/g is lower than that of evaporation for pure water (2260 Joule/g). Estimation of  $\Delta H_{ev}$  at various  $N$  for two peaks with changing the number of water molecules was carried out. At high  $N$  (15-20) the decrease of  $\Delta H_{ev}$  is defined an action conformational transformations for seven-member rings. At low  $N$  (5-7) the main contribution in the decrease of  $\Delta H_{ev}$  is due to the effect of amide groups on the net of hydrogen bonds between water molecules causing its weakening.

# ORDERING AND NANOSECOND MOBILITY IN MACROMOLECULES OF WATER-SOLUBLE POLYMERS UPON METAL IONS ADDING\*

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## Introduction

The effect of ions of polyvalent metals on the structure of water-soluble polymers in aqueous solutions and the effect of intramacromolecular structure formation upon forming macromolecular metal complex (MMC) on MMC stability, determined by the portion of metal ions connected with polymer chains by large duration contacts were studied by polarized luminescence. Polymers with covalently attached luminescent labels were used [1 - 4].

The investigation of the structure formation in macromolecules upon the interaction between metal ions and macromolecules in aqueous solutions is carried out on the basis of analysis of changes in relaxation times,  $\tau$ , characterizing nanosecond relaxation processes in polymer chains, since nanosecond relaxation times are highly sensitive to the intramacromolecular structure changes in solution. Nanosecond relaxation times were determined by polarized luminescence.

The influence of intramacromolecular structure formation being due to MMC formation on MMC stability in aqueous solutions was studied by using luminescently marked polymer-competitor added in MMC solution. The change of MMC stability was determined by the change of portion of metal ions passed from MMC on a polymer-competitor, and was evaluated by using a calibrating dependence characterizing the change of intramacromolecular mobility of a polymer-competitor upon interaction with metal ion determined by polarized luminescence.

## Results and discussion

It was found that at the interaction of water-soluble polymers containing anionic groups with polyvalent metal ions, i.e. upon MMC formation, the intramolecular compact structure was formed and the intramolecular mobility of polymer chains was decreased (Fig. 1a). The data obtained show the dependence of the intramolecular structure formation upon the interaction between metal ions and polymer chains on the time of the interaction between them, on the content of anionic groups in polymers and on that of ions of polyvalent metal in solution, on pH and ionic strength of solution (Fig. 1a, b).

We obtained for the first time the data showing the increase of the stability of MMC with the time of the interaction between metal ions and polymer chains. At the high content of anionic groups in polymers the MMC stability in the course of MMC forming enhances at the initial stages of MMC forming, at the low content of anionic groups in polymers the enhancement of MMC stability occurs smoothly in the wide interval of the time. The molecular mechanism of the influence of polymer chemical structures on MMC stability was established.

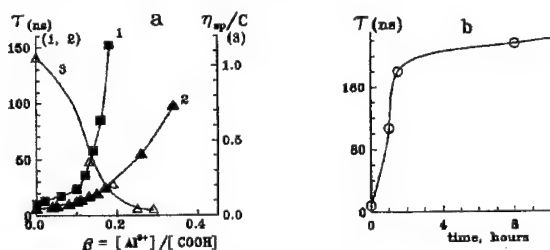


Fig.1.  $\tau$  vs.  $\beta = [\text{Al}^{3+}]/[\text{COOH}]$  (molar ratio) for polyacrylic acid (1);  $\tau$  and  $\eta_{sp}/C$  vs.  $\beta$  (2, 3) (a) and  $\tau$  vs. time of MMC formation (b) for copolymer acrylamide-acrylic acid (74:26 mol.%) in aqueous solutions; pH 7.6; polymer concentration = 0.0003 g/g; 0.5 M NaCl; 25°.

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## DYNAMIC PROPERTIES OF POLYMER CHAINS IN SOLUTION AND SUPRAMOLECULAR STRUCTURE FORMATION

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The interaction between iso- and atactic polymethylmethacrylates (PMMA) in solution was investigated by polarized luminescence. Luminescent labeled PMMA samples with covalently attached luminescent groups of anthracene structure were used. Polarized luminescence permits us to determine the changes in the relaxation times both of iso- and atactic PMMA upon interaction separately. It is known that relaxation times are sensitive to any changes in structure organization of polymer chains [1, 2].

It was established that interpolymer complexes (IPC) are formed in the solution containing iso- and atactic PMMA at a low polymer concentration ( $< 0.1\%$ ). IPC possessing the network structure are formed in a good solvent. On increasing polymer concentration and time of the interaction the solutions are gradually transformed to the gel [3]. It was established that relaxation times characterizing the intramolecular mobility (IMM) of polymer chains in IPC were closed to those in a weakly crosslinked and branched atactic PMMA [4].

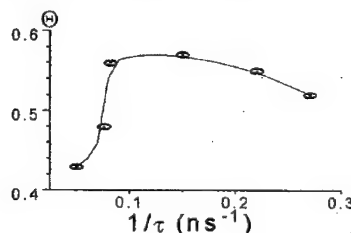
The influence of changing the chemical or topological structure of atactic PMMA chains on the interaction between atactic and iso- PMMA was studied. The effect of introducing the methylacrylate (MA) unites (3 - 20%) in the PMMA chains on the relaxation times both of individual PMMA chains and those in IPC in solvents of various thermodynamic quality was established. It was shown that at low content of MA units ( $< 9\%$ ) in polymer chains the efficiency of IPC formation as compared to that of for interacting homopolymers increases. At further increasing content of MA units ( $> 15\%$ ) IPC formation hinders even though a poor solvent used.

The effect of decreasing IMM of PMMA chains by changing their topological structure upon crosslinking polymer chains on IPC formation was also studied. The relaxation times are varied from 4 ns to 20 ns. It was established that increasing relaxation times from 4 ns to 12 ns does not affect the interaction between iso- and weakly crosslinked PMMA in a good solvent. The further increasing relaxation times of PMMA leads to decreasing efficiency of interaction.

These results give possibilities for widely varying IPC properties by weakly changing the structure of interacting macromolecules and show the functional importance of the nanosecond dynamics of polymer chains in the intermolecular interactions and supramolecular structure formation.

**Table.** Changes of  $\tau$  and  $\Theta$  in time (t) upon the interaction between atactic and iso-PMMA in dimethylformamide.  $\Theta$  is a portion of atactic PMMA chains included into IPC upon their interaction with iso-PMMA  
[a-PMMA]/[iso-PMMA]=3,0;  $C_{pol}=0,013$  g/g; 25°C.

t, hours	$\tau$ , ns	$\Theta$
0	2.5	0
1	4.8	0.55
24	5.6	0.7
48	9.7	0.74
72 (gel)	11.7	0.79



**Fig.**  $\Theta$  vs  $1/\tau$ .  $\Theta$  is a portion of crosslinked PMMA chains included into IPC upon their interaction with iso-PMMA in dimethylformamide.  $\beta = [\text{crosslinked PMMA}]/[\text{iso-PMMA}] = 1,0$ ;  $C_{pol} = 0,008$ g/g; 25°C.

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## PHASE SEPARATION IN POLYMER-PARTICLE-SOLVENT SYSTEMS

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Two regimes of phase separation in polymer-particle-solvent systems are considered theoretically, namely, due to incompatibility and due to complexformation between polymer and small particle. The regimes are characterized by different components distribution between two macroscopic phases: in the former, each phase includes almost all amount of one of the macro-components and traces of another, while in the latter, one phase includes stoichiometric polymer-particle complex, and the other one, an excess of one of the macro-components.

Critical values of the polymer-particle interaction parameter for the regimes are estimated depending on d.p. of a polymer and size of particles. For incompatibility, the parameter is of order  $+0.01kT$ , and for complexation,  $-0.1kT$ . So, the transition from one of the regimes to another should occur in the narrow interval of external conditions variation.

Two kinds of the systems are studied experimentally. Both systems form a continuous gel at high concentrations of macro-components, a (colloid) solution at low concentration of one of them, and two macroscopic phases elsewhere; the borders between these three cases vary on variation of pH. We used concentrations of macro-components corresponded to two-phase case at all pH values.

In the system poly(N-vinyl pyrrolidone) - sol of poly(silica acid) (PSA), a stoichiometric complex stabilized by H-bonds is shown to be formed in acidic media, while in neutral and alkaline ones, incompatibility takes place. A transition between two regimes is found to occur at pH 6.0-6.5, it's regularities being in agreement with the theoretical predictions.

In the system poly(2,5-dimethyl-N-vinyl pyridinium methylsulfate) - PSA, a stoichiometrical complexformation was expected in alkaline and neutral media, while in acid one, incompatibility was expected due to change in the sign of surface charge of PSA particles. Nevertheless, in the whole investigated pH-range (0.5-8.0) neither stoichiometrical complexformation, not incompatibility were not found. In all the experiments, one phase contains only the polymer, and another, both macro-components, their ratio being dependent on the initial concentrations. The results obtained for this system may be considered as a consequence of (i) non-stoichiometric complexformation, and (ii) reversible adsorption of macromolecules on small particles.

# BEHAVIOUR OF COPOLYMER OF DIVINYL ETHER WITH MALEIC ANHYDRIDE IN WATER AND ACETONE SOLUTIONS

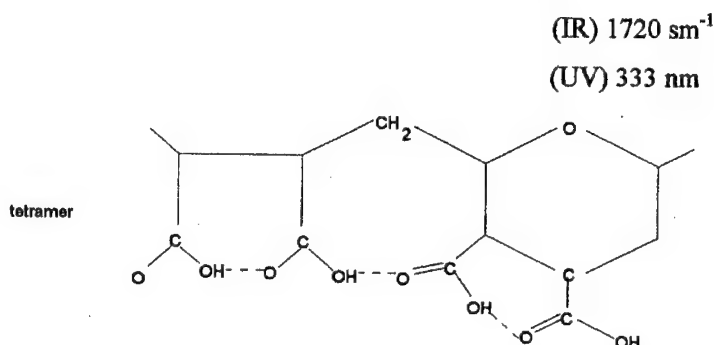
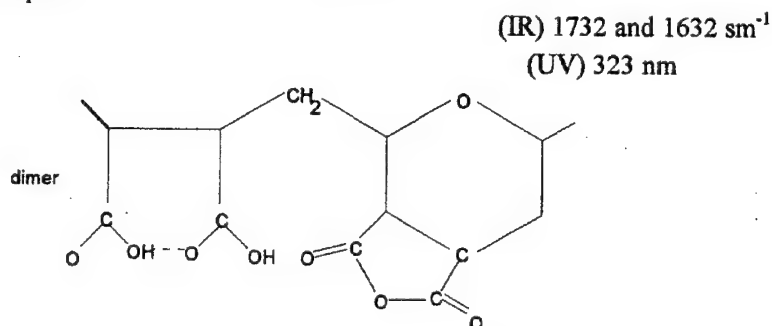
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Interaction of copolymer of divinyl ether with maleic anhydride (DIVEMA) with the solvent (water and acetone) was studied by spectral methods (UV and FT-IR).

The hydrolysis kinetics of DIVEMA in neutral aqueous media was studied. It was demonstrated that complete dissolving of the copolymer was possible only if 56% of anhydride units were hydrolysed. The study of DIVEMA stability in acetone revealed that 30% of anhydride groups were hydrolysed in 2 hours even if acetone had dried previously ( $C_{H_2O}=0.05$  mol/l).

In solution carboxylic groups took part in the formation of intramolecular H-bonded dimers or intramolecular H-bonded linear polyassociates of not more than four carboxyl groups which was demonstrated by simulation with molecular models. Electron delocalization in H-bond associates visualised by electron spectra.



This phenomenon was more pronounced in linear tetramer than in dimer which made the tetramer more stable. It could be assumed that as a result of this association DIVEMA macromolecules became more compact.

Obviously polymer ionisation (carboxyl groups neutralisation by NaOH) caused tetramer destruction and macromolecules expansion as a result of single-charged groups repulsion. The change in macro molecule conformation was demonstrated by specific form curves of DIVEMA potentiometric titration.

Thus H-bonded tetramers in DIVEMA solutions are responsible for increased chain rigidity with possible diminishing of segment mobility if polymer was hydrolysed for more than 30%.



## REORGANIZATION OF WATER-SOLUBLE POLYAMIDE STRUCTURE INDUCED BY WATER

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Some polymers (for example, poly(ethylene oxide)) show unusual mixing properties with water. In the past few years these effects were attributed to the behavior of water confined to small regions within polymers. As is known, the strong hydration of poly(ethylene oxide) is mainly induced by topological effects inasmuch as within the chain conformation of this polymer the distance between the ether oxygens is almost coincident with that of water oxygens. However, similar effects are well studied for the limited range of polymer-water systems only. In this respect, the discovery and investigation of different systems with such properties give the possibility of achieving new information on this peculiar organization of matter.

Water-soluble polyamide was prepared by condensation of ethylene diglycolic acid - piperazine salt. The bulk poly(piperazine ethylene diglycolamide) (PPEDGA) slowly crystallizes and it is characterized by intense sorption of water. The wide-angle and small-angle X-ray scattering, calorimetry, equilibrium water sorption, kinetics of sorption and sound velocity measurements have been applied for study of this polymer and polymer-water systems.

PPEDGA is characterized by three regimes of water sorption. In this case, a continuous decrease of its glass transition temperature takes place. When the water content is increased a change of the polymer crystal structure occurs. Upon sorption, the water molecules are distributed in very thin layers between PPEGDA chains, and under the action of hydration forces the spatial and temporal evolution of the system occurs. As a result, the macromolecules change their conformations and the structural transition takes place. Thus, one deals with the formation of the PPEGDA - water complex. These results are in agreement with the measurements of hydration numbers by the sound velocity technique.

## **Study of hydrodynamic properties and molecular characteristics of polymethacryloyl glucose samples in dilute solutions**

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In order to establish the effect of vinyl fragments position in vinylsaccharide on the molecular characteristics of polyvinylsaccharides, a comparative study of samples of methacryloyl glucoseamine homopolymers (PMGA) was investigated. They were obtained from monomers containing a methacryloyl residue in C-3 position (obtained by the polymerization of 3-0-methacryloyl-1,2,5,6-diisopropylidene glucose with subsequent removal of protective groups) and in C-6 position (obtained by the polymerization of 6-0-methacryloyl glucose which was synthesized in a single stage by using a proteolytic enzyme). PMGA samples were investigated by the methods of molecular hydrodynamics in a 0.1 aqueous solution of sodium acetate at 25 C. In this solvent primary polyelectrolytic effects do not appear. Translational diffusion and sedimentation coefficients and intrinsic viscosity were measured. Refractive index and density increments were determined. The molecular weights of samples under investigations were evaluated on the basis of sedimentation-diffusion analysis. The correlation between molecular weights and hydrodynamic characteristics made it possible to establish the corresponding scaling relationships for PMGA and to evaluate chain equilibrium rigidity. Conclusions are made about the effect of structure on molecular characteristics of PMGA chains.

AGGREGATION BEHAVIOR OF TELECHELIC POLYDIMETHYLSILOXANE  
IONOMERS IN DILUTE SOLUTIONS

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A series of carboxy- and carboxylate-terminated telechelic polydimethylsiloxanes of different molecular weight have been synthesized. The neutralization of carboxy-terminated polysiloxanes with LiOH is found to lead to carboxylate-terminated telechelic polymers formation without the change of their MWD.

Lithium-carboxylate telechelic ionomers have been studied by static light scattering and vapor phase osmometry in the low polarity solvent toluene. These data demonstrate micellization in dilute solutions. Closed association characteristic features indicate the proximity of critical micellar concentration (cmc). The secondary aggregation of micelles into larger particles which leads gradually to the phase separation of the system is observed via light scattering. Since this process is slower than the former, the aggregation number and radius of micelles can be usually determined. The occurrence of a closed association mechanism for the individual micelles and an open association for larger aggregates can manifest itself in complex aggregation behavior. The secondary aggregation mechanism consisting in network formation of micelles bridged with the chains is supposed in conformity with the theoretical predictions<sup>1</sup>. The influence of the chain length and the average functionality of telechelic ionomers on aggregation behavior is studied.

This research was supported by the Russian Science Foundation (grant 9503-09565).

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**LINEAR AND BRANCHED  
POLY(VINYLPYRROLIDONE). SPECIAL FEATURES  
OF THE CONFORMATION AND MOBILITY OF  
MACROMOLECULES IN SOLUTION**

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Linear and branched copolymers of N-vinylpyrrolidone and allyl monomer with different ratio of monomer units in the chain and different molecular weights had been obtained for the first time.

It was found that these linear copolymers might contain a various number of monomer units (30-100) in chosen experimental conditions. It was supposed that both chemical nature and length of the polymer chain had a large influence on the conformational behavior of these copolymers in solution. For this purpose the comparative estimation of behavior of these copolymers in wide range of concentrations and temperatures was carried out.

Special features of behavior of these branched macromolecules in dilute solution were noted. The non-linear character of the change of viscosity properties may be stipulated by "good" solvent influence on macromolecular swelling. Estimation of the thermodynamic parameters was also carried out.

## PHASE SEPARATION OF POLYMERS IN WATER. TEMPERATURE AND SURFACTANT EFFECT

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Polymers which are soluble in water at low temperatures but insoluble above a critical temperature, the lower critical solution temperature (LCST) have recently received much attention, because their technological and biological significance. The LCST can be conveniently decreased or increased in the presence of some additives. The effect of cosolvents on the LCST has been extensively studied. Also a small quantity of ionic surfactant has a remarkable influence on the LCST due to electrostatic interaction of the surfactants bound to the polymer. In order to investigate the coil-globule state, in this work, the influence of surfactants on the cloud point of poly(N-vinyl-2-pyrrolidone) (PVP) and related copolymers in aqueous solutions was studied. The PVP concentration has a very important role on the effect of the surfactant on the cloud point. In the vicinity and above the LCST intermolecular aggregation occurs even at extremely low concentrations. We found that very small amounts of SDS are sufficient to clarify the solutions above the LCST and that some surfactants shift the transition temperature to a value  $T_c$  which is higher than the LCST of surfactant-free solutions.

Under these conditions, we can study the conformational changes of the macromolecules, in function of the temperature at constant SLS concentration, in a region where the chains were aggregated.

The experimental results about the size of the chain have been obtained by using laser light scattering and viscometric measurements.

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## **The Effect of Glass Transition on Phase Separation Dynamics in Binary Off-Critical Blends.**

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Dynamics of phase separation has been investigated in mixtures of oligostyrene and oligobutadiene that have low concentration of the later. Phase diagram has the upper critical solution temperature and the intersection point with the glass transition line. At temperatures near glass transition temperature, off-critical binary mixtures were found to experience phase separation through the mechanism of very slow hydrodynamic coarsening. Nonequilibrium percolation threshold was shown to take intermediate position between binodal and mean-field spinodal. This experimental observation agrees with theoretical predictions of Binder et al. Below percolation threshold a droplet morphology was produced. Above percolation threshold, a bicontinuous phase structure was produced. At low supersaturations, this glass-like percolation structure breaks down to ramified clusters, and, on long staying, these clusters slowly assume a spherical droplet form. At higher supersaturations, coarsening is accompanied by contraction of the percolation structure to the center of the sample. At late stages, secondary phase separation is observed in the glass-like phase.

These experimental findings has been explained by coupling between concentration fluctuations and viscosity fluctuations since viscosity depends stongly from concentration in this system. At temperatures near glass transition temperature the percolating phase has very high viscosity and very small diffusion coefficient. Besides that the non-zero values of shear modulus arise that result in solidity of perolating network phase.

Off-critical binary mixtures with high concentration of glass-like component phase separate on the scale lower one micron. Therefore this phenomen can be termed as microphase separation.

At first, coupling between phase separation and glass solidification provides a unique opportunity for a detailed characterization of morphological evolution in binary mixtures. At second, this coupling is interesting itself since phase separation induces glass solidificaion of one phase but glass solidification hinders phase separation.

# MICROSEGREGATION IN MIXTURES OF WEAKLY CHARGED POLYELECTROLYTES IN AQUEOUS SOLUTION

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Theoretical treatment revealed that in solutions of immiscible weakly charged polyelectrolytes, both macrophase and microphase separation is possible. As a result of microphase separation, microdomain structures are formed, in which energetically favorable contacts between units of the same polymer are ensured and at the same time ionic interactions between oppositely charged groups of the polymer components are maintained. From experimental point of view studies on microphase separation in the weakly charged polyelectrolyte mixtures could open a new route to creation of special polymer materials with easily controlled microstructures.

The supramolecular structures of the weakly charged polymers in aqueous solution were studied on an example of the system copolymer of acrylamide and vinylsulfonic acid (CPAV) / poly(1-vinyl-1,2,4-triazole) (PVT) / water. The phase diagrams for charged CPAV / PVT / water and corresponding uncharged polyacrylamide PAA / PVT / water systems were obtained. The supramolecular structure of polymer mixtures was investigated by turbidity spectra method. It was shown that supramolecular aggregates of size 0,1 micrometer lay within the range of theoretically predicted for microdomains in mixtures of weakly charged polymers. Supramolecular associates are formed only within the region of macrophase separation of the system and they do not exist in the miscibility region. Such aggregates were observed in both macrophases or in only one of them depending on the initial concentration of polymers.

## THE MOBILITY OF POLYURETHANE MOLECULAR CHAINS

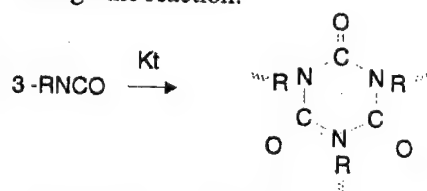
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By thermomechanical curves analysis (TMA) the temperature transitions in polyurethaneisocyanurates (PUIC) were studied. PUIC obtained contain the rigid and flexible fragments being of varying content and chemical structure.

PUIC flexible fragments were formed on the base of a crystal state polyethyleneglycoladipinate (PEA) or an amorphous polyethylenebutyleneglycoladipinate (PEBA) with a 80:20 ratio of ethylene and butylene blocks in olygoester.

PUIC rigid fragments consist of diisocyanate (DI) molecules being partially trimerised through the reaction:



The influence of 2,4-toluenediisocyanate (2,4-TDI), the mixture of isomers - 2,4- and 2,6-toluenediisocyanates in a 80:20 ratio (T 80/20) and a 65:35 ratio (T 65/35), as well as 4,4'-diphenylmethanediisocyanate (MDI) and the mixture of MDI and MDI polymerization products (PI) was also studied. The content of rigid fragments was varied by increasing DI:olygoester ratio within 1,1 and 5,0. Temperature range of between -60 and 350°C was used.

It was noted that in the case of PEA, two low temperature transitions occur. The first one was caused by the glass-to-highelastic PUIC transition. The second one resulted from the melting of a crystalline phase in olygoester. In the case of PEBA, the glass temperature ( $T_g$ ) was much lower compared with that of PEA derived PUIC, and no second temperature transition.

It was showed that PUIC with less content of rigid fragments and less magnitude of effective network density (of about 300-400 mole/m<sup>3</sup>) have had "the retrace of deformation" in the range of glass-to-yield temperature ( $T_g - T_y$ ). This is typical situation for low modulus polymers.

However, in spite of increased network density, the trend of thermomechanical curves at high temperatures seems to be anomalous as the content of rigid fragments increases. The highelastic-to-viscoflowing transition was pronounced slightly because of raised content of large isocyanurate structures, so hindering polymer flow.

DI nature had pronounced effect on both the low temperature and high temperature transitions in going from TDI via MDI to PI. To select the optimum ratio of rigid and flexible fragments as well as their nature, the trends of thermomechanical curves were therefore analyzed. This resulted in real formulations and technological parameters to prepare PUIC systems.



## STRUCTURAL EVOLUTION IN COPOLYMERS OF ACRYLONITRIL WITH METHYLACRYLATE DURING ALKALINE DEGRADATION

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Studies of chemical and morphological transformations of polymer coils in poly(acrylonitrile) solutions and copolymers during the addition of alkali are of a great interest, which is caused by the possibility of simulation of macromolecular reactions and large areas of the applications of these polymers. In this work we have investigated the influence of crosslinking of polymer chains on an intramolecular mobility and alkaline hydrolysis of acrylonitrile-methylacrylate (AN-MA) copolymers in solutions by spectroscopic and viscometric methods. The results of the study demonstrate the correlation of the intrinsic viscosity, the kinetics of UVS and the wave length depending on CN-groups content in copolymers. The increase of MA fraction decreases the mean statistical size length where the process of cyclization of CN-groups can occur, and the probability of intramolecular crosslinking increases. This leads to the restriction of macromolecular mobility and the arising of steric factors hindering of the basic mechanism of cyclization. The polymer coil keeps the ability of compaction during the quantity of CN-groups decreases, but the degree of compaction decreases with decrease of length of cyclic sequences.

# THE STRUCTURE OF THE THERMOREVERSIBLE GELS OF METHYLCELLULOSE IN WATER AND DIMETHYLACETAMIDE AND PROPERTIES OF THE FILMS OBTAINED FROM THEM

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It is known that physical thermoreversible gels based on methylcellulose (MC) can be prepared by heating aqueous MC solutions and by cooling MC solutions in dimethylacetamide (DMAA)[1]. The MC gels in water and DMAA and films obtained from solutions and solutions which were transformed into gels were studied by X-ray method (WAXS).

It has been shown that the type of crystallization centers in MC gels in water and DMAA are various. The size of crystallization centers in MC gels in water corresponds to those of tri-substituted polymer units. The crystallization centers in MC gels in DMAA are unsubstituted and partially substituted MC polymer units. The marked differences indicated that heating of aqueous MC solutions is followed by breaking of interaction between molecules of water and tri- substituted polymer units. On the contrary the cooling MC solutions in DMAA is followed by breaking of interaction between DMAA molecules and unsubstituted or partially substituted polymer units.

The mechanical properties of the films obtained from studied systems were investigated. The tensile strength, elongation on break and Young's modulus of the films obtained from MC solutionc in DMAA were shown to be higher than those of the films obtained from aqueous MC solutions. The MC solutions transformation in gels with following evaporation of solvents leads to the increase of mechanical properties of films in both cases.

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# **SUPERMOLECULAR ORGANISATION OF THE SOLUTIONS MIXTURES OF CHITIN AND CELLULOSE IN COMMON SOLVENT**

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The supermolecular structure of the semidiluted (3% w) solutions mixtures of chitin and cellulose in common solvent -dimethylacetamide with LiCl (9% w) was studied by method of polarized light scattering. The interpreting of obtained results was carried out on the base of statistical theory of Debye-Stein. The supermolecular structure of solution mixtures had been characterized with next parameters:  $a_v$  and  $a_H$  - correlation radiuses of polarizability fluctuation and orientation,  $\overline{\Delta C^2}$  - the mean square of concentration fluctuations,  $\overline{\delta^2}$  -the mean square density of the anisotropy of scattering volume elements.

The obtained data indicate the drastic changing associative structure of the solutions of polysaccharides at introduction of small amount of other polysaccharide. It was shown that small amount of cellulose introduced into solution of chitin (or chitin into solution of cellulose) leads to drastic increase of intensity isotropic and anisotropic components of light scattering. This fact reflects the increase of the fluctuations of concentration, anisotropy and orientation in the solutions. As hole the dependencies of the parameters  $a_v$ ,  $a_H$ ,  $\overline{\Delta C^2}$ ,  $\overline{\delta^2}$  versus composition of mixtures have complicated configurations with maximums and minimums. This indicated the formation of fluctuational anisotropic associates in semidiluted solutions. Those associates can be nucleus of the supermolecular structure which influenced the properties of materials in the solid state.

# DETERMINATION OF THE RATE CONSTANT FOR CHAIN INSERTION INTO POLY(METHYL METHACRYLATE)-BLOCK-POLY(ACRYLIC ACID) MICELLES

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Poly(methyl methacrylate)-block-poly(methacrylic acid) (PMMA-b-PMAA) with and without pyrene labels, attached to the end of the PMAA block, have been synthesized and characterized. These polymers formed micelles with PMAA as the core in ethyl acetate/ methanol mixtures, if the ethyl acetate volume fraction is higher than 80%. After mixing a micelle solution of PMMA-b-PMAA without pyrene labels, i.e. Polymer I, with a unimer solution of the sample with pyrene, i.e. Polymer II, the fluorescence intensity  $I_{Py}(t)$  of pyrene increased with time. This was caused by the insertion of the pyrene group of Polymer II chains into the rigid core of Polymer I micelles. Pyrene fluorescence Quantum yield is higher in a more rigid environment due to the reduced quenching of pyrene fluorescence by oxygen and the possible suppression of certain non-radiative deactivation pathways. A kinetic model was proposed for describing the chain insertion process. Fitting the experimental fluorescence intensity data using the derived expression for  $I_{Py}(t)$  allowed the first determination of the rate constant  $k_{in}$  for diblock copolymer chain insertion into micelles.

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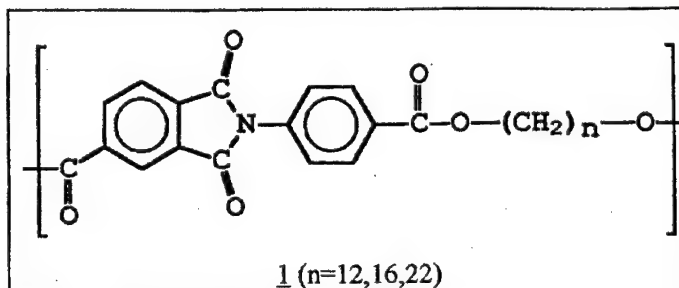
## SMECTIC-SPHERULITIC - A NEW MORPHOLOGY

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Poly(ester imide)s (PEI) of the chemical structure **1** form smectic layers due to micro-phase separation of the polar rigid imide-mesogens and the non-polar flexible alkane-spacers. In this connection it should be emphasized, that smectic phases can be either liquid-crystalline (LC) or true-crystalline in the solid state. The

regular sequence of mesogens and spacers give rise to a middle-angle X-ray reflection  $2\theta=2-8$ . While PEI with short spacers ( $n<12$ ) form LC-phases which transform into smectic-crystalline phases upon cooling, PEI



with long spacers ( $n>12$ ) crystallize directly from the isotropic melt in a smectic-crystalline phase. Simultaneous measurements of wide-angle X-ray scattering (WAXS) and middle-angle X-ray scattering (MAXS) reveal, that the crystallization and the formation of the layer structure coincide, both following an Avrami-kinetic with an exponent of  $n=3$  during an isothermal process. Thus, a formation of a three-dimensional super-structure can be proposed. Actually, micrographs between crossed polars exhibit a spherulitic superstructure. Spherulites of normal semi-crystalline polymers consist of lamellar stacks of crystalline and amorphous regions and the long period gives rise to a small-angle X-ray scattering (SAXS). Surprisingly, this smectic-crystalline PEI ( $n>12$ ) show a SAXS as well, while the PEI with short spacers, crystallized from the LC-phase, do not.

These observations lead to a model for a new type of morphology which can be named smectic-spherulitic. It describes spherulites built by lamellae of 100-400 Å thickness which in their part consist of 3-10 smectic layers. Contrary to semi-crystalline polymers the change of SAXS is reversible upon heating and cooling for the smectic-spherulitic polymers, indicating a high mobility even in the crystalline state (meso-phase character). With increasing temperature the SAXS shifts to smaller angles reversibly due to an expansion of the lamellae by tipping of smectic layers. Taking a closer look at the SAXS-curves they actually turn out to be a series of maxima and shoulders. Moreover, the shift of the SAXS does not take place continuously but results from increasing and decreasing of discrete reflections. They correspond to lamellae with integer number of smectic layers.

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## **SHEAR-INDUCED ORDERING IN NEMATOGENIC COPOLYESTERS**

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We report study on films of main-chain liquid crystalline copolyesters based on mesogenic units of 4,4'-bis (4-hydroxybenzoyloxy) biphenyl and aliphatic spacers of different length. Films were produced from melt subjected to shear, and subsequently were annealed. Various textures formed were studied by means of 'full-contrast' polarizing microscopy, laser-light scattering and measurements of transmitted light intensity. Arrangement, dimensions and inner structure (director orientation) of the banded-type textures are dependent upon spacer length. The results obtained are related to model theories of the relaxation properties of macromolecules in liquid crystalline state.

## ORIENTATIONAL ORDERING OF POLYMER AT POLYMER-LIQUID CRYSTAL INTERFACE

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It has been known that supermolecular ordering in low-molecular liquid crystals in the vicinity of polymer-LC interface essentially depends on supermolecular structure of contacting polymer [1]. The present paper seeks to demonstrate the capacity of liquid crystals, in turn, to exert some ordering effect on polymer supermolecular structure. The subject of experimental study were polyvinyl alcohol (PVA) films encapsulated LC-droplets. LC-droplets of micrometer size were nearly spherical and contained nematic LC (bipolar configuration of director field within the droplet) or nemato-cholesteric composition (more complex director field configurations). Cyanobiphenyl mixture SZK-1 with nematic-isotropic liquid transition at 63°C was used as nematic LS. The same mixture with 1.1% of L-menthol as chiral dopant was employed as nemato-cholesteric composition. It had 3.8  $\mu\text{m}$  natural pitch of the helix and LC-isotropic liquid transition at 60°C. 15-20  $\mu\text{m}$  thick films were obtained through the LC emulsion in 10% PVA water solution.

With the aid of microscopic measurements there were compared the deformations of nematic and nemato-cholesteric droplets after special heat treatment of the films that led to uniaxial orientation of polymer with practically uneffected sample dimensions [2]. In the course of film formation from emulsion at room temperature, nematic and nemato-cholesteric LCs are in mesophase and have substantially higher supermolecular order and lower molecular mobility than PVA in solution.

On PVA-LC interface, tangential boundary conditions occur, *i.e.* director field lines lie in phase boundary. Here, mean director line length / droplet radius ratio value for nemato-cholesteric droplet exceeds value of the parameter for pure nematic droplet.

On the assumption that the supermolecular structure of polymer in the vicinity of interface follows, in the course of evaporation of the solvent and film formation, director field configuration of LC-droplet we should expect higher degree of deformation of the droplet in the case of nematic than for nemato-cholesteric mixture. Experimental results obtained prove this assumption. Average degree of deformation (aspect ratio) is 1.24 for nemato-cholesteric droplets and 1.09 for nematic droplets.

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## **STRIPE DOMAINS IN LIQUID CRYSTAL ELASTOMERS**

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0HE**

Liquid crystal elastomers are networks formed by crosslinking liquid crystalline polymers. Frequently these elastomers are oriented during crosslinking to form networks with a uniform director orientation.

A very successful microscopic theory of the behaviour of these Monodomain elastomers has previously been developed and shown to successfully predict and explain many important experimental phenomena.

Recent experiments on elastomers have shown that under certain conditions an oriented (Monodomain) sample may on extension develop stripe domains, with a characteristic width, these then disappear on a further extension.

We show here that the basic microscopic theory of Liquid Crystal Elastomers predicts the formation of such domains, the angles of director rotation within the domains and their subsequent disappearance on further extension. However we find that factors such as compositional fluctuations and orientation of crosslinks together with end effects, which would ordinarily have only a small effect on the free energy of the rubber, are important in setting thresholds for the formation of the stripes as well as their characteristic size of the domains.

We will also discuss the possibility of other non-uniform deformations occurring in these materials.



## STRUCTURE AND PHASE TRANSITIONS OF POLYPHOSPHAZENES WITH SIDE GROUPS CONTAINING ALKYL MOIETIES

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Data on phase transitions and structure of crystalline phases and mesophases in poly(dialkoxyphosphazenes)  $[N=P(OC_nH_{2n+1})_2]_x$ , partially fluorinated poly(dialkoxyphosphazenes)  $[N=P(OCH_2(CF_2)_mCF_2H)_2]_x$ , and poly(dialkylamino-phosphazenes)  $[N=P(NHC_nH_{2n+1})_2]_x$  with different length of alkyl moieties (from  $C_1$  up to  $C_{16}$ ) in the substituents are presented.

The trend of polyphosphazene macromolecules to exhibit various levels of self-organization (from perfect three-dimensional crystalline phase up to "columnar" mesophase or condiscrystals) is discussed in the context of a compromise between intermolecular dipole-dipole interaction of the inorganic main chains and most favorable packing of side groups. The length of alkyl moiety and the type of the bridge (-O-, -NH-) connecting these alkyl fragments with P atoms are suggested to be main factors which determine the side substituents packing.

Starting with heptoxy-derivative, polyalkoxyphosphazenes behave similar to crystallizable comb-like macromolecules. They crystallize having planar *all-trans* conformation of methylene side chains and *cis-trans* conformation of -P=N-bonds in the main chain. Shorter side groups seem to lend themselves to form ordered domains of a symmetry close to the hexagonal one. In the case of partially fluorinated polyalkoxyphosphazenes this results in arising along with low-temperature usual crystalline phases high-temperature polymorphs which are characterized by the hexagonal packing of partially conformational disordered side groups and by the full loss of conformational order in the main chain. The trend of the alkyl side groups to realize the hexagonal packing appears also to be a reason of the unusual transition in poly(dibutoxyphosphazene) and poly(dipentoxyphosphazene) from the mesomorphic state into amorphous one upon cooling to low temperatures.

The formation of hydrogen bonds between -NH- groups in polyaminophosphazenes is an additional driving force to their self-organization. An interplay between the hydrogen bond formation and the packing of side groups strongly affects their phase behavior.

# STUDY ON THERMODYNAMICS AND KINETICS OF MESOPHASE FORMATION IN COMB-LIKE LIQUID CRYSTALLINE POLYCARBOSILANES

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Side chain liquid crystalline polymers consist of a backbone attached through some flexible hydrocarbon "spacer" to liquid crystal mesogenic groups in the side chain to form a "comb-like" structure. Such polymers are of considerable interest as potential material for a variety of applications in physical optics and display technology, especially in relation to reversible information storage devices.

The side chain liquid crystalline polycarbosilanes were prepared in the course of hydrosilylation of mesogenic alkene with the linear polycarbosilane. The results are concerned with an analysis of the thermodynamics and kinetics of mesophase formation by cooling from the isotropic state of side-chain liquid crystalline polycarbosilanes containing spacers in the range from 3 to 11 CH<sub>2</sub>-groups. The polymers are characterized by their thermotropic behaviour as far as temperature, enthalpy and entropy of the transitions are concerned. The kinetics was followed by optical and calorimetric methods. Longer spacer length leads to more perfect ordering in the mesophase, higher isotropization temperatures and lower transition temperatures. The Avrami and Ozawa formalism to describe the transition kinetics to the mesophase from the isotropic state cannot be interpreted as the nucleation and growth mechanism known from crystallization.

## Monte-Carlo Simulations of Low- and High-temperature Phases of Poly (p-hydroxybenzoic)acid.

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The structure and dynamic properties of poly (p-hydroxybenzoic) acid (PHBA) in the low- and high-temperature phases have been investigated by using Monte-Carlo (MC) simulations .

MC simulations of the equilibrium structures of the PHBA low- and high-temperature crystal phases have been carried out for the model system of 64 molecular fragments packed in the orthorhombical (low-temperature phase I) and in the hexagonal (high-temperature phase III) lattice with the experimental values of the crystal cell parameters and with the periodical boundary conditions in the direction orthogonal to the chain axes. The layer structure in the direction of the chain axes is supposed.

The dynamics of the molecular fragments such as the phenyl rings and crankshaft-type fragments in the equilibrium states have been studied by MC simulations as well.

The orientational distributions and the correlation functions of the orientations of the chain fragments for the low- and high-temperature equilibrium structures of the PHBA crystal phases have been obtained.

The comparison of the results of the simulations of the equilibrium structures of the low- and the high temperature phases of PHBA shows strong decrease of the intermolecular rotational correlations for the high-temperature phase. The decrease of the rotational correlations in the high-temperature phase is especially strong for the phenyl rings.

The results of the investigation of the dynamics of the phenyl rings and the crankshaft-type fragments demonstrate the possibility of the flipping motion of the phenyl rings and the rotation of the crankshaft-type fragments with large amplitudes in the high-temperature phase.

These results are consistent with the results of the experimental study of localized motions occurring in the the PHBA homopolymer over a wide range of temperatures.

This work was carried out with the financial support of the INTAS grant 94-4404 and the RFBR grant N 96-03-3383 a.

## CONTINUAL MODEL OF STRUCTURAL PHASE TRANSITIONS IN MACROMOLECULES

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The explicit expression for the polymer chain structural form-factor in the crystal phase, taking into account the conformation mobility effects considered in the framework of macromolecular chain continual model is discussed. For a fairly anharmonic polymer crystal the structural transition presents the phonon dynamics averaged by the chain conformations, while for a heavily anharmonic crystal this is the soliton-like excitation dynamics also averaged by the chain conformations. The phenomenological theory of Landau allows to make a successful description of any experimental data for any type structural transitions. The microscopic theories of structural transitions in polymer systems should give an opportunity of calculating the parameters of Landau theory, taking into account the macromolecular chain structure and their conformational mobility. We would like to discuss the structural form-factor, which gives the phonon peak, reflects the structural peculiarities of the transition and takes into account the flexibility of the polymer chain.

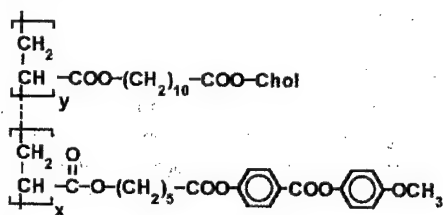
A determination of the structural form-factor for the phonon subsystem is done by the consequent conducting of the two operations: the temperature averaging according to Gibbs and the averaging according to the chain conformations. An adequate mathematic object is the Green function which is responsible for longitudinal shifts of the chain links and its peculiarities (the real and imaginary parts of the poles) determine the spectrum of the collective excitations of the polymer chain in the condensed medium.

## Study of phase behaviour and optical properties of blends of cholesteric copolymers.

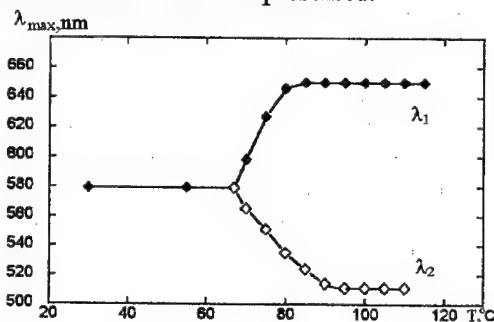
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The synthesis of cholesteryl-containing liquid crystalline (LC) copolymers of the different compositions and molecular mass (copolymers A and B) as well as, the study of phase behaviour and optical properties of their blends are presented.



Copolymers: A:  $y=23$  mol.%,  
B:  $y=38$  mol.%,



We have studied the following systems:

1. Blends of the cholesteric copolymers A and B with  $M_w > 10^4$ .
2. Blends of the cholesteric copolymers A and B with  $M_w < 10^4$ .

All copolymers display the cholesteric mesophases which selectively reflect the visible light ( $\lambda_{\max}$ ). The pitch of the helix ( $P$ ) of copolymers A does not depend on the temperature. Copolymers B are characterized by the negative temperature dependence of  $\lambda_{\max}$  ( $dP/dT < 0$ ).

On the base of the study of phase behaviour and optical properties of copolymer blends their phase diagrams were plotted.

The phase diagram of system 1 characterized by the minimum critical point of mixture ( $T_{\text{cryt}}$ ), above which the microphase separation into two cholesteric mesophases with the different helix pitches takes place. Fig., presented here shows the temperature dependence of the maximum of selective light reflection of system 1 containing the equal (wt %) ratio of copolymers. It is seen that the values of wave length of selective light reflection of  $\lambda_1$  and  $\lambda_2$  correspond to different helical supermolecular structures which are formed in the system 1 as result of microphase separation on the supramolecular level. Below the  $T_{\text{cryt}}$  only one peak of selective light reflection is observed.

Thus, one can reversibly affect the helix pitch of the blends of cholesteric copolymers changing the temperature and obtaining bimodal or unimodal curves of the selective reflection of light.

The copolymers with low molecular mass (system 2) are mixed without any separation at all temperatures. In this case maximum of selective light reflection lies between two maxima inherent to initial components and fits to the average content of the chiral (cholesteryl) groups.

The work was supported by the Russian Foundation of Fundamental Research (Grant, 1996) and HCM Programme of the EC Commission (Contract ERBCITDCT 940602).

## Molecular order in dendrimers with a few terminal mesogenic groups

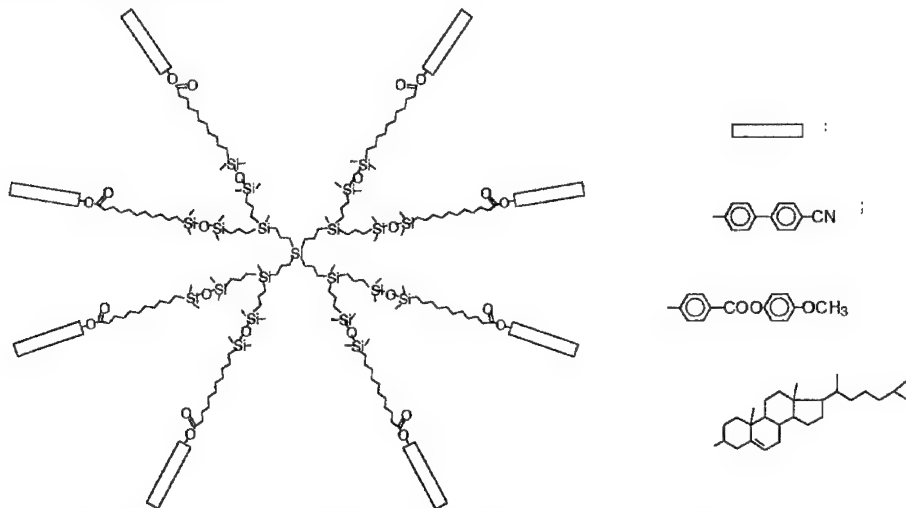
S.A.Ponomarenko\*, E.A.Rebrov\*\*, N.I.Boiko\*, A.Yu.Bobrovsky\*, A.M.Muzafarov\*\*, V.P.Shibaev\*

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In this presentation a comparatively new class of liquid crystalline (LC) compounds - LC dendrimers is considered. These dendrimers are fascinating class of oligomeric and polymeric systems with unique molecular structure. They can be considered as the high-branched or star-like molecules with strictly determined dimensions and molar mass as well as with desirable terminal groups.

Recently we have elaborated an approach to the synthesis of polysiloxane and polycarbosilane LC dendrimers [1,2]. It implies the controlled layer-by-layer technique for dendrimers' growth, mesogen- and spacer-containing groups being used for surface layer only. This paper is devoted to the study of molecular order and LC properties of some polycarbosilane dendrimers with terminal mesogenic groups (cholesterol, cyanobiphenyl and methoxyphenylbenzoate) of the following chemical structure:



The phase state of LC dendrimers investigated has been characterized by the polarizing microscopy and DSC methods. X-ray measurements in combination with computer simulations were applied for molecular order study.

The results obtained show that despite unusual structure the dendrimers bearing a few mesogenic groups exhibit usual liquid-crystalline properties forming smectic-type mesophases. This, probably, is explained by the tendency of side branches to the layer packing. Fan-shaped or schlieren textures in dependence of mesogen groups' type are displayed. They have  $S_A$  or  $S_C$  mesophase in the broad temperature range (approximately 100°), which can be frozen in glassy state at low temperatures. Molecular packing in these mesophases is discussed and presented.

This research was supported by the Russian Foundation of Fundamental Research (grant 1996) and HCM Programme of the EC Commission (Contract ERBCITDCT 940602).

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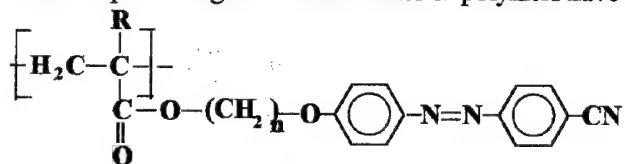
## Photochromic liquid-crystalline homo- and copolymers of acrylates and methacrylates with 4-cyanoazobenzene mesogenic groups.

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Photochromic liquid-crystalline (LC) polymers with mesogenic side groups (comb-shaped liquid crystal polymers) are of considerable scientific interest due to their numerous possible technical applications. The covalent incorporation of the photo-responsive azobenzene chromophores in a polymer matrix leads to the new dye-containing photochromic polymer materials, optical properties of which can be easily and reversibly controlled by using polarized light.

In this work we describe a synthesis, thermal properties and structure of two series of mesogenic azo-dye-containing polyacrylates and polymethacrylates with different spacer length. The new series of polymers have the general formula:



$n = 2-11$   $\text{R} = \text{H}, \text{CH}_3$

As is seen mesogenic groups consist of the photoactive azobenzene fragments bearing the strong CN- dipole providing the high value of dielectric anisotropy. Such molecular structure makes these polymers electro- and photoactive ones suitable for the technical application.

Using the radical polymerization of corresponding monomers only oligomeric polyacrylates and polymethacrylates were obtained. Degree of polymerization (DP) was changed between 10- 50. The samples with higher DP= 200- 300 were synthesized by polymeranalogous reactions with of polyacryloyl and polymethacryloyl chlorides with corresponding 4-cyanoazobenzene aliphatic alcohols.

All oligomers and polymers display the LC phases of nematic and smectic A types. The influence of the spacer length and DP of the samples synthesized on the mesophase types and thermal transitions is discussed.

It is shown that the oligoacrylates with  $n \geq 3$  display smectic mesophases, as the oligoacrylates with  $n = 2, 4$  and  $6$  also form nematic mesophases. Oligomethacrylates with spacer length  $n = 2$  is characterized by nematic mesophases, but oligomethacrylates with  $n \geq 3$  form smectic mesophases. The polymers with DP= 200-300 of both homologous series with  $n = 2, 3$  and  $6$  display smectic mesophases. The transition temperatures between mesophase and isotropic melt of oligoacrylates and oligomethacrylates have tendency to odd-even alternation.

Two series of copolymers containing 20 and 40% of azobenzene fragments and cyanobiphenyl mesogenic groups with the similar spacer length were synthesized. Their DP, thermal properties and mesophase types are determined and discussed.

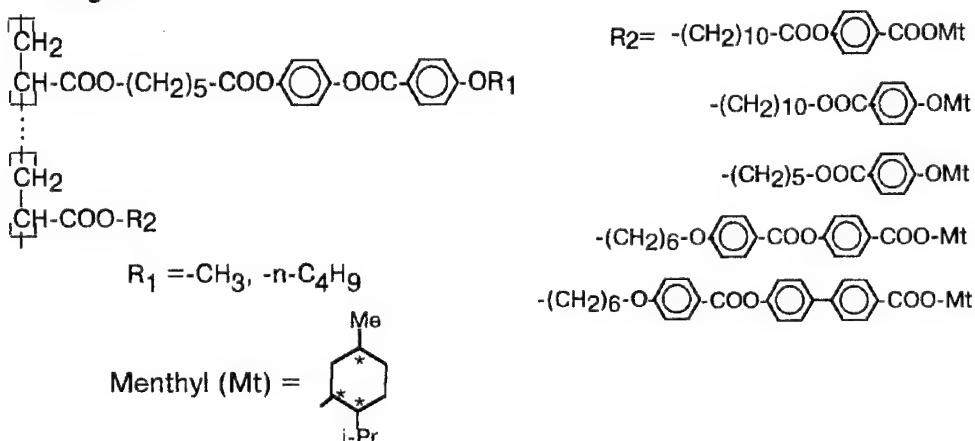
This research was supported by the Russian Foundation of Fundamental Research, 1996 and HCM Programme of the EC Commission (Contract Grant, ERBCITDCT 940602.).

## Chiral mesophases of new menthylcontaining copolymers.

**A.Yu.Bobrovsky, N.I.Boiko, V.P.Shibaev.**

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New menthylcontaining chiral copolymers are synthesized and the influence of chiral monomer units of the various structure (such as, for example, a length of rigid aromatic fragment and spacer length) on some thermal and optical properties of chiral mesophases induced in nematic and smectic matrixes is investigated:



All copolymers display selective reflection of light in visible, IR or near UV- regions of the spectrum. It is shown that one can easily regulate the physical properties of these systems by variation of copolymer composition and the type of monomer chiral units. In such a way we have managed to obtain a number of helical mesophases, such as  $N^*$ ,  $N_B^*$ ,  $N_{cyb}^*$ ,  $S_A^*$ ,  $S_F^*$ ,  $N_{Re}^*$ , and different types of blue phases.

The analysis of experimental data concerning molecular structure - properties relationship permitted to make the following conclusions:

1) The increase of spacer length of chiral groups results in decrease of helical twisting power of chiral component, however the LC temperature interval of copolymers becomes broader.

2) The replacement of the ester group, connecting the chiral center with aromatic fragment, on the ether one reduces the helical twisting power and the temperature interval of mesophase existence.

3) The lengthening of the rigid aromatic fragment not only stabilizes the induced mesophase and increases the helical twisting power, but leads to the smectic ordering if even homopolymers of initial comonomers do not form the smectic phase.

This work was supported by the Russian Foundation of Fundamental Research (Grant 1996) and HCM Programme of the EC Commission (Contract ERBCIPDCT 940602).



# Novel Binaphthyl-Containing Liquid Crystalline Copolymers Forming Chiral Nematic Phase.

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T. Bjørnholm<sup>3</sup>, K. Schaumburg<sup>3</sup>, K. Bechgaard<sup>4</sup>.

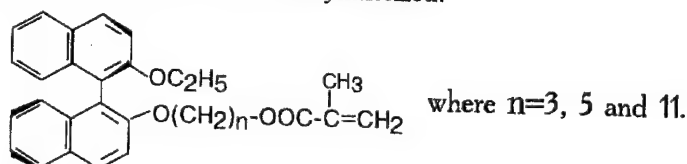
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<sup>3</sup>Department of Chemistry, University of Copenhagen, DK-2100, Copenhagen, Denmark;

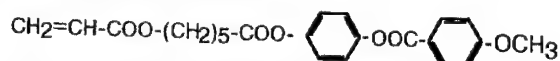
<sup>4</sup>Department of Solid State Physics, Riso, National Laboratory, DK-4000 Roskilde, Denmark.

Chirality has become one of the most important topics in low molar mass and polymer liquid crystal research today. The existence of many types of mesophases, such as cholesterics, chiral smectics, blue phases, twist grain boundary phases is due to chirality of their molecules. The origin of chirality is usually an asymmetric carbon atom [1]. Another source of chirality originates from hindered rotation about single bonds that may lead to two conformationally stable atropoisomers. This type of chirality is usually designated as atropoisomerism [2]. Whereas the chiral low molar mass liquid crystals, chiral monomers and chiral polymers have been well studied, chiral monomers based on atropoisomerism have not been synthesized and used in order to obtain the chiral polymers.

In this report we present and discuss our recent experimental data concerning synthesis and study of the novel chiral liquid crystalline (LC) copolymers chirality of which is based on the atropoisomerism. We therefore focus on the use of this type of chirality using binaphthyl derivatives. These molecules consist of two  $\beta$ -naphthyl moieties connected in the 1,1'-positions with restricted rotation about the C1-C1' bond connecting two aromatic systems. On the base of optically pure (S)-2,2'-dihydroxy-1,1'-binaphthyl three new methacrylic monomers have been synthesized:



These binaphthylcontaining monomers were copolymerized with nematogenic methoxy-phenylbenzoate acrylic monomer:



and such a way three series of copolymers differed in spacer lengths and in their compositions were obtained.

It was shown that all copolymers with a low concentration of binaphthyl (BN) monomer units display a cholesteric mesophase. The helical twisting power (HTP) caused by atropisomeric units in the synthesized copolymers was determined, and its temperature dependencies were studied. The unusually high negative of temperature coefficient of HTP above  $T_g$  was explained in terms of conformational changes of BN fragments in the copolymers.

This work was supported by the Russian Foundation of Fundamental Research (Grant 1996) and HCM Programme of the EC Commission (Contract ERBCIPDCT 940602).

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# Comb-Shaped Liquid Crystalline Ionogenic Copolymers: Synthesis, Phase Behavior, and Mobility in External Electric and Magnetic Fields

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The study of liquid crystalline (LC) polymers containing functional groups capable of forming the inter- and intramolecular H-bonds is of a considerable fundamental and practical interest. In such complicated systems one can combine the specific features of both LC polymers and ionomers leading to new type of materials. This paper describes synthesis of new LC ionogenic copolymers, the study of their phase behavior and orientational mobility in the external magnetic field.

A number of LC ionogenic copolymers of different composition were synthesized by radical copolymerization of cyanobiphenyl containing mesogenic monomer and acrylic acid.

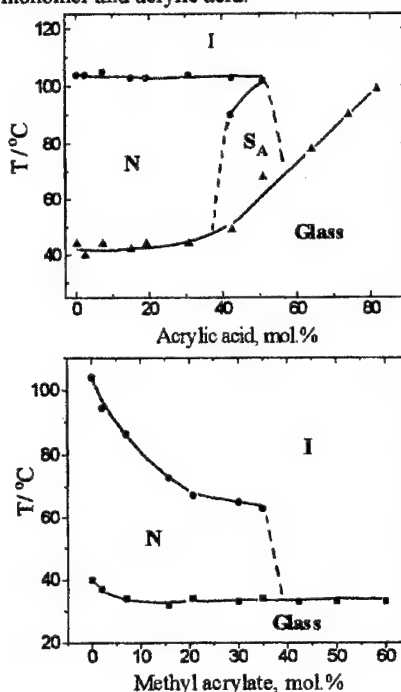
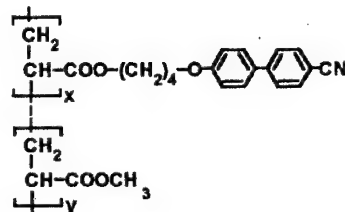
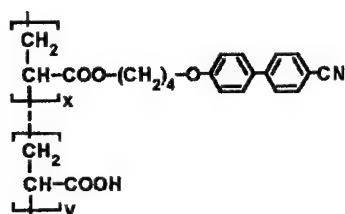


Fig. The chemical structures and phase diagrams of LC copolymers.

The incorporation of the small amounts of acrylic acid in macromolecules of initial nematic polymer does not change the mesophase type of homopolymer. The completely another situation is realized at the higher concentration of acrylic acid (>40 mol.%), when the S<sub>A</sub>-phase formation is observed.

To understand an influence of the H-bonding on the phase behavior of the LC ionogenic copolymers a number of LC copolymers, containing the same mesogenic fragments (4-cyanobiphenyl) and methyl ester of acrylic acid have been specially synthesized. In these copolymers the H-bonds can not be formed and due to this fact only the nematic phase was observed in concentration region less then 35 mol.% of methyl acrylate. Comparison of two types of copolymers shows that the H-bonding interaction leads to the higher thermostability of liquid crystalline phase and to formation of a more ordered S<sub>A</sub> phase.

Orientalional behavior of such systems in magnetic field by broad-line <sup>1</sup>H NMR spectroscopy was studied. The decrease of the order parameter S for nematic copolymers with increase of acrylic acid (till 30 mol.%) was observed. The electrooptical properties of LC ionogenic copolymers were studied and electrooptical characteristics such as orientational time and threshold voltage were determined.

This research was supported by the Russian Foundation of Fundamental Research, (1996) and HCM Program of the EC Commission (Contract ERBCITDCT 940602).

# PREDICTION OF THE TWISTING POWER OF CHIRAL PROBES IN LIQUID CRYSTALS AND LIQUID CRYSTALS POLYMERS

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The presence of chiral centres in nematic liquid crystals and liquid crystal polymers is known to induce twisted mesophases, characterized by helical structures having a pitch of the order of thousand molecular diameters. As a consequence of the supermolecular organization, these materials exhibit special optical effects at the wavelengths of the visible light: pseudo-Bragg reflection, and strongly enhanced rotatory dispersion.

In order to interpret the twisting power of specific chiral dopants, a theoretical model based on the molecular shape has been derived [1]. A surface tensor, which determines the alignment of the chiral probe in the liquid crystal phase, and a helicity tensor which accounts for its chiral features, are defined. Magnitude and handedness of the pitch of the twisted mesophase can be calculated in terms of the strength of the orienting torques and macroscopic elastic constants.

The model has been tested for a series of binaphthyl derivatives in open and bridged forms, dissolved in thermotropic nematics, and the excellent agreement between model predictions and experimental data provides evidence for the important role played by the molecular shape. Extension of the model to liquid crystal polymers with side-chain mesogenic units is discussed.

[1] A. Ferrarini, G.J. Moro, and P.L. Nordio, *Molec. Phys.*, 87, 485 (1996).

Work supported under PECO-NIS Project N. 940602

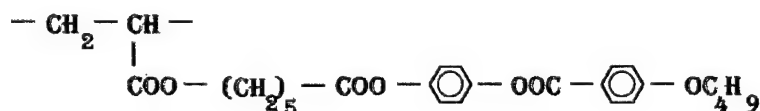
# ELASTIC DEFORMATIONS IN THE MAGNETIC FIELD OF THE NEMATIC PHASE OF SIDE-CHAIN POLYMER

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Elastic deformations in a magnetic field have been investigated for uniformly oriented layers of the thermotropic side-chain polymer nematic having the following structure



$$M_w = 52000 \quad M_w/M_n = 2.0$$

The phase transition temperatures were determined by combined DSC and polarizing microscopy: the melting point  $T = 42^\circ\text{C}$  and the clearing point  $T = 127^\circ\text{C}$ . The polymer exhibits a stable nematic phase in the temperature interval from  $65^\circ\text{C}$  to the isotropization temperature.

The temperature dependences of the optical anisotropy and the bend ( $K_3$ ) and splay ( $K_1$ ) elasticity constants were investigated. The values of  $K_3$  and  $K_1$  were determined from the independent experiments for the homeotropic and planar textures correspondingly.

It was shown that the values of the optical anisotropy (hence of the orientational order parameter) of the polymer nematic under investigation increased practically twice whereas the relative temperature  $\Delta T = T - T_{NI}$  ranged from  $-1^\circ\text{C}$  to  $-65^\circ\text{C}$ .

Elastic constants coincide by the order of magnitude with those for low-molecular-mass and polymer nematics studied previously. It was found that the values of  $K_3$  are some lower than the values obtained for the bend elastic constants  $K_1$  within the temperature range studied ( $K_3/K_1 \sim 0.8$ ).

This work was supported by the Russian Foundation of Fundamental Investigations (grant 96-03-33863a).

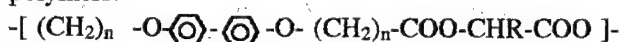
# MOLECULAR CHARACTERISTICS OF MESOGENIC POLYMERS WITH COMBINED AND LINEAR STRUCTURES IN A DILUTE SOLUTION

V.N.Tsvetkov, S.V.Bushin, E.P.Astapenko, E.V.Belyaeva, V.V.Zuev

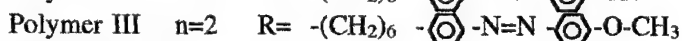
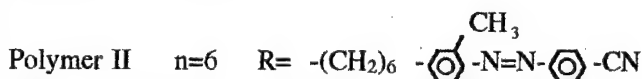
Institute of Macromolecular Compounds, Russian Ac. Sci.

199004 St.Petersburg, Bolshoy pr.,31.

The Hydrodynamic (translational diffusion coefficient  $D$  and intrinsic viscosity  $[\eta]$ ) and conformational properties of molecules in solution have been investigated for three polymers:



Polymer I  $n=6$   $R= -H$



The Mark - Kuhn ( $M - K$ ) dependences  $[\eta]=K\eta M^a$  and  $D = K_D M^b$  for Polymers II and III in a  $\Theta$ -solvent, dioxane at 20 °C, are specific and are characterized by the exponents  $a=0.2$  in the range of  $M \leq 8 \cdot 10^3$  and  $0.4$  in the range  $8 \cdot 10^3 \leq M \leq 33 \cdot 10^3$  and the exponent  $b = 0.46$  over the entire  $M$  range.

These dependences are not characteristic of common flexible-chain polymers to which polymer I belongs ( $a=b=0.5$  in a  $\Theta$ -solvent, chloroform at 20 °C).

These specific dependences of  $M - K$  for polymers II and III reflect the character of intramolecular hydrodynamic interactions, which is typical of branched and comb-like polymers. That result of this character of interactions is the great relative value of the hydrodynamic diameter ( $d/A \approx 1$ ) of the wormlike chain. For polymers II and III the length of Kuhn segment  $A = (20 \pm 3) \cdot 10^8$  cm obtained from data on translational diffusion coincides with that found for polymer I. This fact implies that steric interactions between side groups of polymers II and III have virtually no effect on chain rigidity.

This conclusion is confirmed by the analysis of the values of  $S = A/\lambda$  (equal to 0.6 in the case of polymers I and II and 1.1 in case of polymer III,  $\lambda$  is the monomer unit length). This analysis shows that  $S^{-1}$  is a linear function of the number of methylene groups in the main chain and the value of the hindering factor of rotation about methylene bonds is characteristic of a simple polymethylene chain.

This work was supported by the Russian Foundation of Fundamental Investigations (grant 96-03-33863a).

# FLOW BIREFRINGENCE AND INTRAMOLECULAR ORIENTATIONAL ANISOTROPIC ORDER IN SOLUTIONS OF ALKYLENE-AROMATIC POLYESTERS.

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S.A. Didenko\*\*, V.N. Tsvetkov\*\*

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The method of flow birefringence was used to investigate a number of alkylene-aromatic polyesters with different lengths of flexible methylene fragments in the chain. The dependence of the shear optical coefficient of polymer solutions on the length of flexible fragments in their macromolecules was detected. The problems related to the optical effects of the micro- and macroform of the molecules in the systems being investigated are discussed. It was established that the optical anisotropy of the Kuhn segment experiences not only the general tendency to decreasing with increasing length of flexible fragments in the macromolecule but also certain oscillations when the number of  $\text{CH}_2$  groups in the methylene fragments changes from the odd to the even value. These relatively weak oscillations are caused by changes in the degree of intramolecular orientational anisotropic order in the molecules of alkylene-aromatic polyesters. It is shown that the experimentally determined values of optical anisotropy of the Kuhn segment in alkylene-aromatic polyesters are in good correlation with the calculated values.

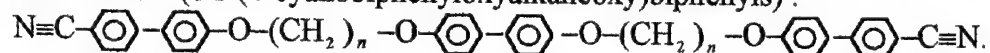
This work was supported by the Russian Foundation of Fundamental Investigations (grant 96-03-33863a).

# ORIENTATIONAL ORDER AND ELASTIC DEFORMATIONS OF NEMATIC TRIMERS IN AN ELECTRIC FIELD.

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The method of orientational elastic deformations in electric fields [1] was used to study electro-optical and dielectric properties of nematics of the trimer series (bis-(4-cyanobiphenyloxyalkaneoxy)biphenyls):



The number  $n$  of  $\text{CH}_2$  groups in methylene spacer was varied from  $n=2$  to  $n=10$ . A dramatic odd-even effect in optical anisotropy  $\Delta n = n_e - n_o$  of the nematics of trimers under investigation was detected. This effect is due to the oscillations of the degree of *intermolecular* orientational order  $S$  during the variations in  $n$ . The values of the threshold electric deformation potential  $V_0$  of monodomain planar textures and dielectric anisotropy  $\Delta\epsilon$  of trimers also exhibit a strong odd-even effect. This effect is mainly caused by variations in the degree of *intramolecular* orientational-polar order during changes in  $n$ . The great difference in dependencies of  $\Delta n$  and  $\Delta\epsilon$  on  $n$  was found. At all even  $n$  the value of  $\Delta n$  (hence, the degree of intermolecular orientational order  $S$ ) is greater than that at odd  $n$ . In contrast, at each replacement of even  $n$  by odd  $n$  the positive  $\Delta\epsilon$  increases. The results are compared with data obtained by us previously for dimers (bis-(4-cyanobiphenyloxyalkanes)) [2, 3].

This work was supported by the Russian Foundation of Fundamental Investigations (grant 96-03-33863a).

[1] V.N. Tsvetkov, N.V. Tsvetkov, L.N. Andreeva, *Polymer Science*, Vol. 35, 238 (1993).

[2] V.N. Tsvetkov, N.V. Tsvetkov, S.A. Didenko, V.V. Zuev, *Mol. Cryst. Liq. Cryst.*, Vol. 265, 341 (1995).

[3] N.V. Tsvetkov, V.N. Tsvetkov, V.V. Zuev, S.A. Didenko, *Mol. Cryst. Liq. Cryst.*, Vol. 265, 487 (1995).

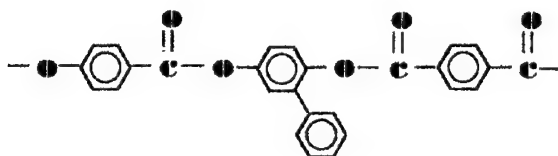
# CONFORMATIONAL CHARACTERISTICS AND MOLECULAR ORDER IN THE CHAINS OF PARA-AROMATIC POLYESTERS

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Aromatic polyesters so as aromatic polyamides have great importance for their ability to show liquid crystal properties. And so both of them are used for very high-strength synthetical fibre materials.

This work deals with aromatic polyester with following structure:



It is soluble only in the mixture of acids: (14.4% monochlor- acetic + 35,5% dichloracetic + 50.1% threechloracetic)acid.

Hydrodynamic and optical properties of para-aromatic polyesters were investigated by viscometry and flow birefringence methods.

Experimental results are compared with those for polyesters of similar structure and polyamides studied before. Investigated macro-molecules shows rigid worm-like chains behavior.

This work was supported by the Russian Foundation of Fundamental Investigations (grant N 96-03-33734a).



# ORIENTATION OF THE NAPHTHYLENE RING IN THE NEW POLY(NAPHTHYLENE-1,3,4-OXADIAZOLE)S MOLECULES

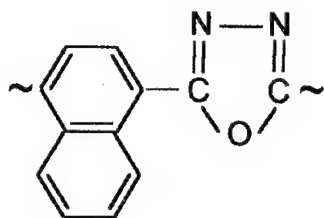
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<sup>1</sup>*Institute of Macromolecular Compounds, Russian Academy of Sciences,  
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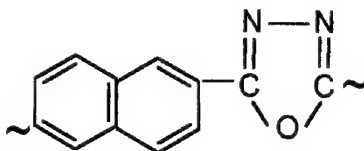
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New heteroarylene derivatives of poly(1,3,4-oxadiazole) (POD) have been synthesized and investigated: poly[(1,4-naphthylene)-2,5-diyl-1,3,4-oxadiazole] (**PNOD-1**) and poly[(2,6-naphthylene)-2,5-diyl-1,3,4-oxadiazole] (**PNOD-2**) where the naphthylene rings (instead of the *p*-phenylene ones in the POD chain) are regularly alternated with the oxadiazole rings:

**PNOD-1**



**PNOD-2**



These polymers have poor solubility in many solvents. Therefore, in this work, solute properties of PNOD-1 and PNOD-2 were investigated in conc. sulfuric acid. Molecular-weight dependence of the intrinsic flow birefringence  $[n]/[\eta]$  and the form effects were taken into account to evaluate the  $[n]/[\eta]$  value in random limit provided by the intrinsic optical anisotropy of the macromolecule.

Flow birefringence data show that optical shear coefficient for these polymers differs significantly from that known for POD in the same solvent. Polarizability of the naphthylene ring is known to have the lowest value in direction perpendicular to the ring plate. Thus, sign and the value of its contribution to the segment anisotropy were used to determine the preferable naphthylene ring orientation in relation to the macromolecule principal axis. Hindrance to intramolecular rotations and changes in equilibrium flexibility of the chain induced by the naphthylene rings incorporation will be also discussed.

The work was supported in part by the International Science Foundation and the Russian Government through the ISF-RFFI project.

# TEMPERATURE-EFFECTED MESOGEN MOBILITY IN WORMLIKE LIQUID-CRYSTALLINE POLY(PHENYLBENZOAT METHYLSILOXANES)

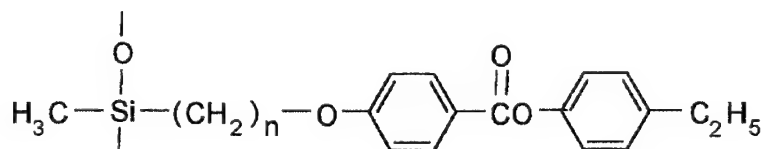
**Peter Lavrenko<sup>1</sup>, Natalia Yevlampieva<sup>2</sup>, Olga Okatova<sup>1</sup>,  
Galina Kolbina<sup>1</sup>, Michael Olbrich<sup>3</sup>**

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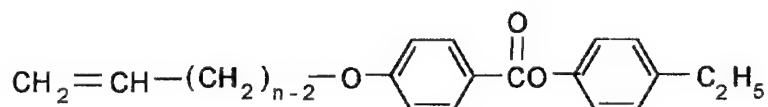
Poly(phenylbenzoat methylsiloxanes), **P4-P11**, with different alkyl spacer groups (from 4 to 11 C-atoms) and corresponding low-molecular-weight compounds, **M4-M11**, as models suitable for the macromolecule side chains, have been synthesized and investigated.



**P4**     $n = 4$

**P6**     $n = 6$

**P11**    $n = 11$



**M4**     $n = 4$

**M6**     $n = 6$

**M11**    $n = 11$

Transition temperatures for the LC phases have been determined. Mobilities of the mesogens and the macromolecule as a whole in dilute solution were studied in an external fields (electric and mechanical shear one). Temperature effects are discussed.

The work was supported in part by the Russian Foundation for Fundamental Investigations.

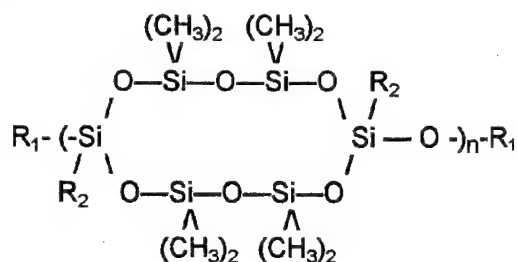
# POLAR AND ELECTROOPTICAL PROPERTIES OF LIQUID CRYSTALLINE POLYDECAMETHYLCYCLOHEXASILOXANE AND ITS LOW MOLECULAR ANALOGUES IN SOLUTIONS

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By the methods of electrooptical Kerr effect and determination of dipole moments in solutions there were investigated two samples of polydecamethyl-cyclohexasiloxane (PDMCHS) with different molecular weight and some oligomeric samples of cyclohexasiloxanes:



PDMCHS:  $\text{R}_{1,2} = -\text{CH}_3$ ,  $n = 56, 80$ ; oligomers:  $\text{R}_{1,2} = -\text{CH}_3, -\text{OH}, -\text{C}_6\text{H}_5, -\text{OC}_8\text{H}_{17}$ ,  $n = 1, 3, 5$ .

It was shown that dipole moments of oligomers and polymers in solutions in tetrachlormethan increase with increasing of hexasiloxane cycle number. It was confirmed a strong dependence of dipole moment values of this class substances upon the thermodynamic quality of the solvent. It was not detected a noticeable influence on dipole moment values of *cis-trans*-locations and chemical structure of side substituents ( $\text{R}_{1,2}$ ) for oligomeric molecular weight cyclohexasiloxanes in solutions.

It was experimentally determined that electrooptical specific Kerr constants dependence on molecular weight reaches its saturation for polymer-homologues series of PDMHCS in oligomeric region of molecular weights. That behavior is typical for flexible-chain polymers. From the value of electrooptical specific Kerr constant in gaussian region of molecular weights an estimation of optical anisotropy of PDMHCS monomer unit has been done.

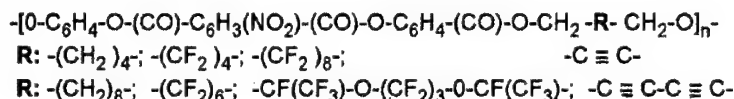
It is known that cyclolinear polyorganosiloxanes form a thermotropic mesophases which type and thermal boundaries depend on the chemical structure of side substituents. As it was shown in the present work an optical anisotropy of polarizability of hexacyclosiloxane ring is very small and its dipole moment value weakly depends on chemical structure of side radicals. Thus, these factors do not play a basic role in formation of mesomorphous properties of polycyclohexasiloxanes.

# MOLECULAR CHARACTERISTICS AND MESOMORFIC PROPERTIES OF AROMATIC POLYESTERS WITH NITRO- GROUP IN MESOGENIC FRAGMENT

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Some aromatic polyesters (PE):



with nitro- (NO<sub>2</sub>) group in mesogenic fragment and different chemical structure of spacer R were synthesized. Mesomorphic properties of PE were studied by polarizing microscope and differential scanning calorimetry methods. Nematic liquid crystalline phase of fluorocontaining PE was founded. The decreasing of the temperature of phase transition from solid to liquid and from isotropic to nematic state as compared with that for PE without NO<sub>2</sub> group was established. Molecular characteristics of fluorocontaining PE in dichloroacetic acid were investigated by viscosity and electric birefringence (EB) methods. Molecular weight of these polymers was calculated from intrinsic viscosity value of PE with the using of Mark-Kuhn's equation for some aromatic PE in same solvent. Equilibrium rigidity  $S \sim 2,3 - 2,8$  ( $S$  - number of monomer units in Kuhn's segment) was estimated with the using of Kerr effect theory in solutions of wormlike chains from the point of sign inverse of the dependence of Kerr constant on molecular weight. The dipole orientation mechanism of PE molecules in electric field was established from the measurements of EB in alternating field. Dependence of the times of orientational relaxation of EB in PE solutions on molecular weight was founded. The introduction of NO<sub>2</sub> group to the mesogenic fragment of fluorocontaining PE leads to the decreasing of the temperature of phase transition from nematic to isotropic melt. The study of molecular characteristics of fluorocontaining PE shows that the equilibrium rigidity of their molecules is more than that of alkylen-aromatic PE with similar mesogenic fragment noncontaining of NO<sub>2</sub> group.

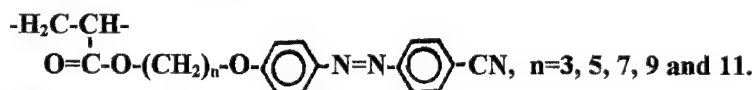
The authors are grateful to Russian Foundation of Fundamental Researche (Grant 94-03-08816) for financial support. □

## Dielectric relaxation in oriented LC comb-like polyacrylates with 4-cyanoazobenzene mesogenic side groups.

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Dielectric method was used to study a number of LC comb-like polyacrylates with the following general formula:



The scientific interest in these polymers is determined by unusual optical properties which may be reversibly changed by laser illumination.

In the range of low temperatures ( $T < T_g$ ) two dielectric processes were found -  $\gamma$  (at the lowest temperatures) and  $\beta$  (at more high temperatures). The temperature dependencies of relaxation time  $\log \tau = \varphi(1/T)$  show that in the region of the  $\gamma$  process the mobility of kinetic units rises with the spacer lengthening but in the case of the  $\beta$  process the mobility is not changed. The activation energy of the  $\beta$  process is 17 kcal/mole for all studied polymers but the activation energy of the  $\gamma$  process falls from 17 ( $n=3$ ) to 10 ( $n=11$ ) kcal/mole. Parameters of both these processes point to a local character of molecular mobility: the  $\gamma$  process reflects the motion of spacer groups and the  $\beta$  process - the motion of mesogens. It was shown the orientation of mesogenic groups by electric or mechanic fields did not influence on dielectric behavior at the low temperatures.

Two cooperative processes of dielectric relaxation (the  $\alpha$  and the  $\delta$  process) were observed near the  $T_g$  region. These processes may be attributed to the motion of perpendicular and parallel components of dipole moment of the mesogenic groups. The main contribution to dielectric absorption provides the motion of two polar groups of mesogene - azo- and cyan-groups. The motion of these polar groups is interconnected because the mesogene is kinetically rigid.

The studied polymers were oriented by electric or mechanic fields. Orientation leads to the changing of the intensity of dielectric absorption of the  $\alpha$  and the  $\delta$  processes but the relaxation times and activation energies are not changed. The statement of planar or homeotropic orientation of mesogenic groups is determined both the orientation way and the side chain length of polymer. For oriented samples the parameter order was evaluated.

This research was supported by the Russian Foundation of Fundamental Research (Grant 96-03-33849a).

**DIPOLE MOMENTS OF POLYSILARYLENES WITH  
ESTER AND AMIDEAROMATIC FRAGMENTS.**

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It is very important to investigate the conformational properties of polysilarylenes with amide and ester fragments because the macromolecules of these polymers are able to form the ordering structure in solution and bulk.

The information about the conformational properties of polymers may be received from the studying of dipole moments.

The investigation of dipole moments of polysilarylenes with amide and ester fragments and their low molecular weight analogous was made.

The correlation factors which reflect the correlation of polar groups in macrochain were calculated.

It was shown that the correlation factor in polysilarylene with ester-aromatic fragment is 0.9. This fact indicates that there are no interaction between esteraromatic fragments in polysilarylene with ester fragment.

But in polysilarylene with amide fragment the correlation factor is 1.6. Comparing this value with one for H-bond containing polymers it may be concluded that there are H-bonds on macromolecular level also in polysilarylene with amide fragment. It provides the correlation of polar groups in macromolecular chain.

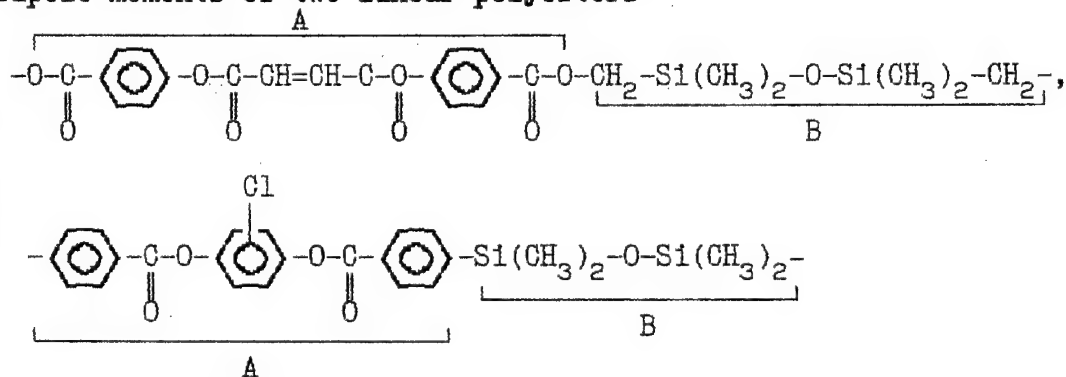
This work was supported by RFFI (Grant N96-03-33849a)

# DIPOLE MOMENTS AND MUTUAL ORIENTATION OF FRAGMENTS IN LINEAR POLYESTERS IN SOLUTION

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Dipole moments of two linear polyesters



and their low-molecular analogs have been measured in dilute solutions in toluene at 20–80°C. Methods of the conformational statistics based on the rotational isomers theory were applied to linear polyesters considered as regular copolymers with several polar components. The correlation factors of dipole moments of rigid fragments (A) in both polymers  $g_{ef} = (\bar{\mu}^2 - n\bar{\mu}_B^2) / n\bar{\mu}_A^2$  were calculated ( $\bar{\mu}^2$  and  $\bar{\mu}_B^2$  are the average squares of dipole moments of a polymer and of a flexible spacer, B; n is a degree of polymerization). For both polymers theoretical and experimental data show that  $g_{ef}$  is almost independent on temperature and its value is close to unity. It is concluded that orientations of rigid groups in the isolated macromolecule are not correlated. The capability of linear polyesters to form liquid-crystalline phase is determined completely by their capability for intermolecular packing which depends on both intermolecular interactions and steric possibilities of the system.

This work was supported by RFFI (Grant N 96-03-33849a)

## Simple and Complex Secondary Relaxations in Linear Polyesters and Polyamides with Siloxane Spacers

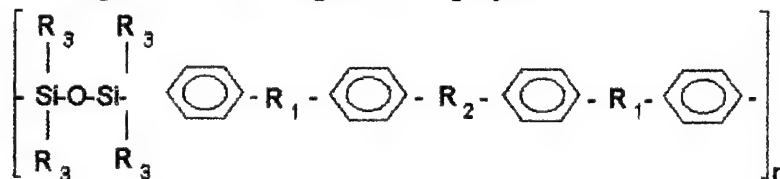
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Below the glass transitions molecular motions in polymers give rise to secondary (subglass) relaxations. These processes take place in all polymers, but their molecular origin is not well understood.

From this point of view it is interesting to study the dielectric relaxation in linear polymers with parts of different rigidity, because regular alternation of rigid and flexible chain's elements determines the existence of various types of intramolecular motions.

We investigate the following kinds of polymers:



The structures variations of  $R_1$  (COO or CONH);  $R_2$  (O; (O-Ph)<sub>2</sub>-O; C(CH<sub>3</sub>)<sub>2</sub>; (CH<sub>2</sub>)<sub>n</sub>, n=2-4) and  $R_3$  (CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub>) enables us to separate the influence of different fragments on the molecular mobility.

The study of dielectric relaxation shows, that marked polymers are characterized by two types of intramolecular mobility:

- 1) The high-frequency movements of extremely short polar elements (ester-phenyl or amide-phenyl groups) are realized with  $\tau \sim 10^{-8} \dots 10^{-6}$  s and  $U \sim 40 \dots 60$  kJ/mole.
- 2) The low-frequency correlative movements the same polar groups with central part of esteraromatic or amidearomatic fragment ( $R_2$ ) are realized with  $\tau \sim 10^{-4} \dots 10^{-1}$  s and  $U \sim 60 \dots 100$  kJ/mole.

The first type of mobility is determined in general by intramolecular local interactions. The second one depends on both sizes of  $R_2$  and intermolecular interactions and doesn't appear when flexible methylene sequence is introduced into the central part of amidearomatic fragment ( $R_2$ ) instead of aromatic groups.

So, the first (simple) relaxations reflects the motion of small molecular fragments, but second (complex) involve cooperative motions more extend part of macrochain.



## **ENOLIZATION OF DICARBONYL FRAGMENTS INCORPORATED INTO POLYESTER MAIN CHAIN**

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Polyterephthaloyldiacetodecanoate containing two coupled tautomer fragments was synthesized. Its keto-enol equilibrium, determined from NMR spectra, is compared with that for monomer model compound terephthaloyldiacetoacetic ester. Reduced enol fraction was found for polymer. This effect can be explained by additional lowering of the chain conformational entropy, caused by steric cis-enol cycles with intramolecular hydrogen bond. It appears also that enolization of the first dicarbonyl fragment in the monomer unit makes difficult enolization of the second. This is due to lesser electronegativity of enol group than ketone one.

(Supported by grant No.95-03-08436 of Russian Foundation of Basic Research).

**FIELD-DEPENDENT STRUCTURAL TRANSITION IN THE SOLUTIONS  
OF MAIN CHAIN LC POLYESTERS.**

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The structure and dynamics in the semidilute and concentrated chloroform solutions of main chain LC polyesters containing fumaroil-bis-oxybenzoate mesogenic units connected by methylene and/or oxyethylene spacers (p(F-M) and p(F-O), respectively) have been the subject of our previous studies [1,2]. Aggregation was shown to proceed in these semidilute solutions leading to the formation of a transient thermoreversible gel, which was destroyed at  $T = 35-40^{\circ}\text{C}$  while heating. However at concentrations below the gel threshold the unusual properties of the solutions are observed in the vicinity of  $T^*$ . The present study deals with the origin of this structural transition at  $T^*$  as studied by proton magnetic and dielectric relaxation, viscometry and UV absorption spectroscopy.

The transition manifests itself in a sharp extremum of the solution viscosity accompanied by a similar and sharp extremum of spin-lattice relaxation times of chloroform and polymer, and by the changes of self-diffusion coefficients of chloroform. Maximum of dielectrical losses is observed at  $T^*$  in p(F-M) solutions. The independence of its position on the frequency of external electric field indicates the structural character of the transition. The dramatic increase of dielectrical losses is observed when the constant electric field is applied across the sample. However, the transition is not observed when methylene spacer is changed to an ethylene oxide one. The comparative analysis of UV absorption spectra of the dilute solutions of p(F-M) and p(F-O) showed the interaction (probably, dimerization) of benzene rings in p(F-M) polymers. In other words, the formation of hairpins even in dilute solutions of semirigid LC polymers can be supported by the spacer rigidity and/or by the solvent quality. Therefore, the most probable mechanism of the field-dependent structural transition in the solutions of p(F-M) is the dissociation of the hairpins.

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## THIN FILMS OF LIQUID CRYSTALLINE POLYMERS

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There are different techniques to study the phase behavior of liquid crystalline polymers (LCP) in bulk material. One can use for instance differential scanning calorimetry (DSC), polarisation microscopy with a hot stage and X-ray scattering. However thin (sub micron range) films have not been studied as extensively as LCP bulk material. External reflection infrared spectroscopy (IR-ERS) has been used by several groups to study the structure, level of orientational order and chemical interaction of several molecules in ultrathin films (2.5 to 500 nm). None of them used liquid crystalline polymers, however.

Reflection infrared spectroscopy at grazing angle of incidence with p-polarised light (electric field oriented normal to the surface) can be done with high sensitivity. In this case, only those vibrational modes which have a component of their dipole moment normal to the surface will interact strongly with the electric field. By comparison with transmission spectroscopy, the orientation of the functional groups of the molecules in the film can be investigated.

In this study a first start is made to use grazing incidence reflection infrared spectroscopy to study the change in order in thin films of thermotropic side-chain liquid crystalline polymers upon a temperature change.

## MECHANICAL PROPERTIES OF LIQUID-CRYSTALLINE COPOLYESTERS

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As illustrated by the behavior of the well-known Vectra A900 from Hoechst-Celanese, the main-chain liquid-crystalline aromatic copolyesters exhibit mechanical properties (tensile modulus, strength) which are comparable to those of glass-reinforced technical thermoplastics.

However, their modulus drops well below the glass transition temperature, as the result of a strong secondary transition which is observed in the room temperature range at 1 Hz. Viscoelastic studies performed in the temperature range  $-150^{\circ}\text{C}$  /  $+150^{\circ}\text{C}$  and in the frequency range 0.01 Hz / 80 Hz allowed to investigate further their unusual transitional behavior. This includes : i) the general observation of a  $\gamma$ -transition at  $-55^{\circ}\text{C}$  (1 Hz), and this, whatever the chemical formula may be, ii) the damping associated with the  $\beta$ -transition which is quite greater than the glass transition damping and iii) the existence of surprisingly high values of the viscoelastic coefficients associated with the glass transition (typically,  $C_1^g = 25$  and  $C_2^g = 80^{\circ}\text{C}$ ).

This peculiar transitional behavior is shown to influence also the mechanisms of plastic deformation in compression mode. To this end, strain-stress curves were determined over the temperature range  $-90^{\circ}\text{C}$  /  $+90^{\circ}\text{C}$  at strain rates ranging from  $2 \cdot 10^{-3}$  to  $0.2 \text{ s}^{-1}$ . The temperature and strain rate dependences of the yield stress are shown to be closely related to the effects of the  $\beta$  relaxation motions.

In conclusion, the effect of the nematic ordering on the mechanical properties of these copolyesters can be understood as the result of their characteristic chain dynamics.

## Mesophase behavior of hydrogen-bond complexes of poly- and dicarboxylic acids with amine hydrochlorides

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A new approach to create thermotropic LC phase based on the general ideas of the lyotropic mesomorphism is suggested. Hydrochlorides of tertiary amines under study behave as conventional amphiphiles forming lamellar phases in water solutions. The change of water by poly- or dicarboxylic acids results in H-bond complexes having the ordered structure. The main feature of the order is the combination of the small angle maximum and amorphous halo in the X-ray patterns indicating the formation of lamellar smectic-like phase in solid complexes. The analysis of the structure in both crystalline and lamellar phases is given. On the base of textured X-ray patterns the model for the layered structure is discussed. The change of the length and the structure of amine residue results in the change of the interplanar spacing in accordance with the model proposed. Low molecular weight models based on glutaric acids show the same tendency to mesophase formation. The phase diagrams of two component systems are studied. The mesomorphic behavior of complexes is interpreted in the terms of microphase separated systems.

This work was supported by Russian Foundation for Fundamental Research (No 94-03-09535). X-ray investigation were carried out according to the program "Universities of Russia".

## INVESTIGATION OF ORDER, MOBILITY AND TRANSREACTIONS AT INTERFACES OF ROD-COIL BLENDS BY MEANS OF WAXS AND NMR

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Blends of the liquid crystalline copolyester oxybenzoate-co-oxynaphthoate (Vectra A) with either PET or isotactic PP were investigated. Such blends consisting of flexible and rod-like molecules tend to phase separate due to entropic reasons. The molecular order and orientation was examined by means of a microfocus X-ray beam with a focal spot of 1  $\mu\text{m}$ . Solid-state NMR ( $^2\text{H}$ ,  $^{13}\text{C}$ ) enabled us to study the molecular dynamics at various temperatures. Moreover, transesterification reactions of the polyesters were detected by  $^{13}\text{C}$ -NMR measurements in solution on  $^{13}\text{C}$ -labeled blend samples.

In blends of Vectra/PET cylindrical LCP domains are embedded in the PET matrix. Upon annealing, epitaxial growth of PET spherulites at the interface is obvious. Extended annealing in the melt results in transesterification which amount is, however, much smaller than in single phase polyester blends. Nevertheless, the transreactions lead to a decrease in the degree of molecular orientation (Vectra) and crystallinity (PET) and to the formation of an interphase with further reduced orientation and crystallinity and, consequently, increased molecular mobility. Furthermore, the Vectra domains adopt a spherical shape, probably due to a reduced melt viscosity.

Vectra and iso-PP have a very poor adhesion and, therefore, show phase separation on a macroscopic scale. No mutual influences of the polymers with respect to their orientation, crystallinity or dynamics were found. Neither, an interphase with modified molecular properties was revealed.

# **SPIN LABELLED LIQUID CRYSTALLINE POLYISOCYANATE. EPR STUDIES ON BULK POLYMER AND SOLUTIONS.**

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Poly(octyl isocyanate), POIC, is one of the alkyl substituted polyisocyanates which show both thermotropic and lyotropic liquid crystallinity. Solutions of POIC are also interesting because some of them form thermoreversible gels.

A spin labelled POIC has been studied by simulating the EPR spectra measured from dry polymer, as well as from POIC dissolved in nonpolar hydrocarbon solvents. The thermal transitions of a fractionated bulk polymer have been studied by DSC; these transitions are observable also as changes in the shape of the EPR spectra. EPR spectra of the dry polymer have a multicomponent character. The spectra have been simulated using an oscillational model of averaging of the magnetic tensors of the nitroxide label; to reproduce the experimental spectra, three various modes of oscillational motion have been combined. The motion of the label has been shown to be intimately dependent on the polymer conformation and thus, the results show that helical and random coil conformations of the polymer coexist in the semicrystalline as well as in the liquid crystalline phase.

The spectra measured from solutions and gels have been simulated using an axially symmetric (rotational) model of averaging of the nitroxide tensors  $A$  and  $g$ . It has been observed that even in nonpolar solvents, the solvent may affect considerably the flexibility of the polymer chain. Aggregation of the polymer chains has been detected as a strong dipolar interaction between the nitroxide radicals in solutions capable of forming thermoreversible gels.

# SCANNING ELECTRON AND ATOMIC FORCE MICROSCOPY INVESTIGATION OF THE MICROSTRUCTURE OF MELT SPUN FIBRES OF THE THERMOTROPIC LIQUID CRYSTAL POLYESTER

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The microstructure of melt spun fibres of poly(oligooxypropylen-200)terephthaloyl-bis-(4-oxybenzoate) with different molecular masses  $\overline{M}_w = 11 \times 10^3$  (I),  $25 \times 10^3$  (II) and  $40 \times 10^3$  (III) have been investigated.

Scanning electron and atomic force microscopy (SEM and AFM) in combination with wide-angle X-ray diffraction (WAXD) have been used.

It has been found, that all fibres under study have a fibrillar morphology and lamellar microstructure, ranging in sizes and degree of alignment depending on the molecular mass. In particular, the fibrils observed in fibres I and II are short and 0,5-2  $\mu\text{m}$  thick, the longer and thinner fibrils (0,14-0,25  $\mu\text{m}$  thick) are found in fibre III.

Melts of polymers I-III have the smectic liquid crystal structure of the "C"-type. Macromolecules of fibres I and II are oriented perpendicular to the fibre direction, whereas those of fiber III are arranged both parallel and perpendicular to the direction of orientation. These data are in agreement with /1,2/.

SEM and AFM results make it possible to propose new microstructure models of polymers under study.

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**STUDY OF GLOBULAR STRUCTURE OF PERSISTENT  
MACROMOLECULE:  
TOROID VS. SPHERICAL GLOBULE**

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It is known that persistent macromolecules in compacted globule state can form toroidal structure, since such macromolecules have no weak points for bending, and wrap themselves circumferentially to minimize the loss of elastic free energy. As a result, a hole is formed in the center of globule, whereas the density of monomers within toroid bulk can be relatively high.

The high attention is paid to the study of toroidal structure since it was found that DNA can undergo transition to the toroidal globule with liquid-crystalline ordering of strands and that such structure is typical for DNA packing in viral and bacteriophage pathogens.

We have studied theoretically the structure of persistent macromolecule in low-molecular solvent. The conditions when the toroidal structure is stable were determined and the diagram of states in variables contour length  $L$  vs. parameter of interaction  $\chi$  was constructed.

It was found that

- (i) Toroidal globule can in principle exist even for very long chain;
- (ii) The density of monomer links within bulk of toroid can be smaller than the most dense packing density;
- (iii) For stiff enough chains coil at first transforms to toroidal globule, and only then to spherical globule;
- (iv) The size of the collapsed macromolecule diminishes upon the transformation from toroid to spherical globule.

The theoretical results were compared with experimental data.

## ***PHASE SEPARATION IN POLYMER NETWORKS***

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Recently several experimental observations on the two-phase structure of polymer gels undergoing collapse transition in various solvents have been reported. The aim of the present work was to investigate theoretically the possibility of the coexistence of two thermodynamically stable phases inside networks. We have evaluated the conditions for realization of phase separation for the following situations:

1. Swelling of polyelectrolyte networks in one-component low-molecular solvents. In this case the coexistence of two phases differing in swelling ratios can take place if the amount of the solvent is not enough to ensure a free swelling. It has been shown that the two-phase region increases considerably with the increase of the degree of ionization of the network.

2. Swelling and collapse of polyelectrolyte networks in solvents containing oppositely charged surfactants actively interacting with the network chains and forming aggregates inside the networks. It appeared that for the case of the lack of the surfactant component in the solvent to form one-to-one complex with polyelectrolyte chains of the whole network the surfactant ions penetrate only in the thin outer layer of the gel. The aggregation of surfactant ions induces the contraction of this layer while the inner part of the gel remains swollen. We reveal the influence of the degree of ionization of the gel and the surfactant concentration on the stability of the phases and calculate their composition.

## **The Dynamical Properties of Polymer Networks with Different Topology.**

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In the works of Gotlib, Salikhov; Klokowski, Mark, H. Frish et al., the existence of two types of molecular motions in polymers networks was shown: 1. intrachain motions and 2. co-operative network motions. In the works of Cerf, Peterlin and de Gennes the inter-segmental interactions in polymers were taken into account by introduction of the internal friction. Further Gotlib suggested to represent the interchain interactions in cross-linked polymers by using two types of friction: 1. the external friction between macromolecules and external medium and 2. the intersegmental and interchain viscous friction.

In this paper the relaxation spectra, time dependence of relaxation modulus and frequency dependence of storage and loss moduli of networks with different topology are under investigation. Both mesh-like and tree-like networks are examined. The influence of interchain friction on dynamic moduli is under study. The parameter of theory is the ratio of interchain friction to external friction coefficients.

The shape of distribution function of the relaxation times in low-frequency region strongly depends on the ratio of interchain/external friction coefficients. The contribution of each relaxation time to distribution function does not depend on topology and is proportional to  $\left(\frac{\tau'}{\tau}\right)^2$ , where  $\tau$  is the relaxation time and the  $\tau'$  is the relaxation time of the same polymer network without interchain friction. The ratio of mean relaxation time to initial relaxation time goes to unit while increasing the parameter of theory. The frequency of maximum of loss modulus of swollen networks shifts to low frequency region with increasing of interchain interaction. The intersegmental friction causes appearance of high-frequency limit of dynamical viscosity. The qualitative character of influence of the parameter of theory on the relaxation properties of polymer networks is similar for all types of network topology.

The asymptotical behaviour of loss and storage moduli of model networks are compared with results of the experimental study of cross-linked actin network performed by Müller et al.

## **The theory of low-frequency dielectric relaxation properties of polymer networks with interchain friction**

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In the recent years the series of experimental papers, which deal with dielectric relaxation of polymer networks, were appeared (Fytas, Kremer, Karatos et al). In the previous theories (Ronka and Allegra, Gotlib and Salikhov, Graessly, Kloczkowski, Mark, Frisch et al) the mechanical dynamic characteristics of polymer networks (dynamic modulus and viscosity) were studied. In the present paper the theory of dielectric relaxation properties is considered for polymer networks built from macromolecules with dipole moment directed along the end-to-end chain vector. The viscoelastic cubic model of regular network with "meshlike" connectivity is used. The fixed average volume of polymer network is taken into account by the introduction of an effective internal pressure. The dynamic network models with only external friction of the chains relative to an effective external medium (viscous matrix) were studied till now. In this paper the dynamic models of polymer networks with external friction and interchain mutual friction, which were suggested by Gotlib previously, are considered. Two limiting cases of the network models are studied: 1). the polar chains are cross-linked in the network at their ends; and 2). a given polar chain in a network contains many network junctions along the chain contour. The relaxation spectrum of autocorrelation function of total dipole moment consists of two regions: the high-frequency intrachain relaxation spectrum of a chain between network junctions and the low-frequency interchain relaxation spectrum, which is determined by cooperative motions of the network chains. In the present paper the low-frequency relaxation spectrum and frequency dependence of dielectric susceptibility are calculated for different dynamic models of the network. The asymptotic behaviour of autocorrelation function at the long times is obtained. The shape of dielectric relaxation spectrum largely depends on the number of cross-links per polar chain and on the relation between external and interchain friction in the system.

This work was carried out with the financial support of the Russian Foundation of Fundamental Investigations, code 96-03-33833a and INTAS Grant 93-2502.

## DEFORMATION AND ORIENTATION OF POLYMER CHAINS IN STRONG MECHANIC OR ELECTRIC FIELDS.

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Statistical properties of a polar polymer chain in a strong electric field of dipole symmetry and for mechanical field, corresponding to the stretching of the ends, have been investigated on the rotational-isomeric model on a tetrahedral lattice. Two types of dipole moments distributions along the chain are discussed: normal to the chain (like polyvinylidene chloride) and along to the end-to-end vector (polyoxypropylene). The average dipole order parameter and the quadrupole order parameter are calculated for unit vectors with different orientation relative to the chain backbone. The fractions of stretched and coiled rotational isomers and of different isomers sequences were obtained.

Dichroic functions (quadrupole order parameter) manifesting in the IR-dichroism are calculated for unit vectors corresponding to three types of vibrations: along the direction of the monomer unit (wagging vibration), along the bisector of the valence angle (bending vibration), and normal to the both (rocking vibration).

Quadrupole order parameter for different unit vectors is obtained also as a function of chain elongation. The results may be applied to study polymer network elongation as to compare with experimental data.

The polarizability induced by an additional weak dipole electric field superimposed on the orienting strong field is calculated as a function of the magnitude of the strong external field. The obtained results are important to calculate the dielectric susceptibility of deformed and oriented polymers.

The results were compared with those for freely jointed chain in the dipole external field and for the rotational-isomeric chain in the quadrupole field.

This work was carried out with the financial support of the Russian Foundation of Fundamental Investigations, code 96-03-33833a and INTAS Grant 93 2502.

ON THE CORRESPONDENCE OF THE TYPES OF PHASE  
TRANSITIONS IN THE TWO-DIMENSIONAL SYSTEMS WITH  
EFFECTS OF EXCLUDED VOLUME WITH THOSE WITH  
ORIENTATIONAL INTERACTIONS.

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The two-dimensional systems with dipole interactions are considered. The correspondence of properties of the coil-globule transition in chains with excluded volume effects and those of the phase transition into an ordered state in two-dimensional multichain systems with orientational interactions is analysed.

It is shown that the propability of survival in the problem of self-avoiding random walks (SARW) and the distribution function of mean-square dimensions of chains in the two-dimensional polymeric systems considered previously have the same asymptotic behavior for corresponding parameters. The relation between the parameters of the systems with dipole interactions and those of the systems with excluded volume is obtained. The critical exponents of the SARW-model describing the behavior of polymer chain in the  $\Theta$  point of the transition coil - globule coincide with the values of the corresponding critical parameters in the systems with orientational interactions.

This work partially was carried out with the financial support of the Russian Foundation of Fundamental Investigations, code 96-03-33833a and INTAS Grant 94-4404.

## THE COMPARISON OF ORIENTATIONAL DIPOLE ORDERING IN THE MULTICHAIN AND MEAN FIELD SINGLE-CHAIN APPROACHES.

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In the two-dimensional multichain system with dipole interactions the long-range orientational order doesn't exist. In this system there is the smooth phase transition from a state with the intermediate "quasi-long-range" orientational ordering into the isotropic state at the characteristic temperature  $T^*$ . In the self-consistent mean field single-chain approach the second-order phase transition into a state with long-range orientational order occurs at the critical temperature  $T=T_c$ .

In both models the transition to the same exponential behavior of the correlation function above the critical point occurs. The correspondence of the characteristic temperature  $T^*$  with the critical temperature  $T_c$  allows to obtain the relation between the parameter of interchain interactions in the multichain model and the parameter of the molecular mean field. The characteristics of the short- and long-range order in both models are compared. At sufficiently large lateral interactions the degrees of local order in both models are asymptotically close one to another. In the case of low ordering the multichain model must be used. The mean field approach can be applied as a good approximation at comparatively short distances, the scale of which depends on a relation between the parameter of the bending rigidity of a chain and the parameter of interchain interactions.

This work partially was carried out with the financial support of the Russian Foundation of Fundamental Investigations, code 96-03-33833a and INTAS Grant 94-4404.

# COMPUTER SIMULATION OF CONFORMATIONAL PROPERTIES AND DYNAMICS OF ORIENTED POLYMER CHAIN

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Conformational microstructure and mobility of model polymer chain with rigid bonds, fixed valence angles and hindered internal rotation in orienting quadrupole field has been investigated by the method of Brownian dynamics. Three-fold internal rotation potential has been used. At the same time conformational microstructure of chain model in quadrupole field has been studied on tetrahedral lattice with three energetically equivalent rotational isomers,  $t$ ,  $g^+$ ,  $g^-$ . The dependencies of fractions of different conformers on the order parameter  $S$  are similar for both models. Slowest decreasing with increasing  $S$  is observed for  $g^\pm g^\mp g^\pm$  fraction which forms a fold and for  $tgt$  and  $g^\pm tg^\mp$  which is included in a "kink". The average rate of conformational transitions does not depend significantly on orientation for the values of  $S$  from 0 up to 0.5. All types of conformational transitions could be divided in two groups: i) fast autocorrelated transitions and ii) slower non-correlated transitions. Latter is divided in two subgroups which have different dependencies on order parameter  $S$ . This work was carried out with the financial support of the Russian Foundation of Fundamental Investigations, code 96-03-33833a and INTAS Grant 93 2502.



## Equilibrium Properties and Spectrum of Relaxation Times for Polymer Chain in Quadrupole Field. Computer Simulation.

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Computer simulation of the polymer chain with hindered internal rotation in the strong external field of quadrupole symmetry has been performed by the method of Brownian dynamics. Statistical properties, local orientational mobility and spectra of relaxation times have been studied. It is shown that the orientation of the chain bonds increases with increasing the magnitude of external field and does not depend on the torsional barrier height. At the same time the order parameter occurs to be a bit less than that for a model of freely jointed chain (FJC) in the same external field.

Increasing the magnitude of quadrupole field (and degree of ordering) influences the local orientational mobility of this model. As for FJC pronounced anisotropy of local mobility has been observed. The orientational relaxation times increase for projections of chain bonds on the field direction and decrease for normal projections. The dependence of both longitudinal and normal orientational relaxation times on the field magnitude is weaker than that for FJC. The dependence of relaxation times on the magnitude of the torsional barrier shows one-barrier nature of transitions across this barrier. The activation energy for these types of transitions is a bit less than the magnitude of the internal barrier  $U_{int}^0$ .

Existence of normal modes (linear combinations of the coordinates of chain bonds) has been checked. In quadrupole field the spectrum of normal modes relaxation times splits into longitudinal and transversal branches. Contrary to the case of dipole field the relaxation times of longitudinal normal modes increase with ordering. Transversal relaxation times decrease with increasing the magnitude of external field as in the case of the field with dipole symmetry. Such a difference in the behavior of longitudinal and transversal motions mainly results from the existence of two different mechanisms of orientational mobility in quadrupole field: motions with small amplitude near the minima of potential energy and transitions across the potential barrier caused by quadrupole field.

## **Tacticity influence on the flexibility of polypropylene in solution.**

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The static and dynamic flexibilities of iPP, sPP and aPP are investigated by Monte-Carlo and Molecular Dynamics simulations on the basis of a realistic (chemical) model of PP. In the static calculations performed on long chains (1000 C atoms in main chain), the solvent is implicitly incorporated through the free energy character of non-local interactions: the latter are explicitly taken into account in the MC calculations. Under  $\Theta$  conditions at 400K, we find that the Kuhn statistical segment of sPP appears somewhat longer than the Kuhn segment of iPP or aPP. In the dynamic calculations, a fragment of iPP or sPP is followed by molecular dynamics in an explicit solvent (modelling carbon tetrachloride). We focus on the  $P_2(t)$  orientational relaxation of C-H covalent bonds given its link to the relaxation time  $T_1$  in  $^{13}\text{C}$  NMR relaxation experiments. Such NMR experiments have precisely been performed on iPP, sPP and aPP in ortho-dichlorobenzene solutions. The local dynamics of isotactic and syndiotactic sequences within aPP can be separately analyzed. Simulation and experimental data on local dynamics will be intercompared.

## COMPUTER SIMULATION OF DILUTE POLYMER SOLUTIONS IN OSCILLATORY ELONGATIONAL FLOW

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The accumulation of strain by the polymer molecules was observed recently in the model of porous medium, namely in the flow cell which represents two arrays of glass cylinders [1]. The behaviour of polymer molecules in such a flow was simulated by the brownian dynamics method. The velocity profile calculated in assumption that the flow modification in dilute polymer solution is negligible was used. In vicinity of the cell symmetry axis the flow can be described as the oscillatory elongational planar flow. The dumbbell with conformation-dependent friction and elastic coefficients was chosen as the model of polymer molecule.

When initial state had corresponded to a gaussian coil the birefringence values obtained in simulation were two orders of magnitude smaller than experimentally observed data for any flow rate. The polymer deformation simply followed the flow oscillations. Simulation didn't show the experimentally observed shift in the position of the maximum birefringence value to the contraction area of the flow. Moreover when the initial state had corresponded to almost completely stretched macromolecule the birefringence rather quickly decreased to very small values corresponding to slightly deformed gaussian coil.

Effect of the form of the velocity profile on the transient and stationary behaviour of the polymer molecules was also investigated.

The possible explanation of the disagreement between the simulation results and experimental behaviour could be a breakage of the symmetry between converging and diverging flows. This breakage can arise from flow modifications by extended polymer chains.

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# MONTE CARLO COMPUTER SIMULATION OF COIL-GLOBULE TRANSITION OF STIFF-CHAIN MACROMOLECULES

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We present preliminary results on the coil-globule transition of stiff-chain macromolecules obtained by means of Monte Carlo computer simulation.

We used the bond fluctuation algorithm in the standard form to perform our simulations. We introduced an additional attractive quasi-Lennard-Jones potential between monomers which are not successive along the chain to model the quality of the solvent. The strength of this potential decreases gradually from its maximal value at a distance of 2 lattice constants to zero at a distance of 3 lattice constants. The stiffness of the chain was modeled by introducing a potential depending on the angle between successive bonds. Chains of length up to 100 monomers were simulated.

We located the  $\theta$ -point for the chains with different stiffnesses and calculated several quantities pertaining to structural and dynamical properties of stiff chains undergoing the collapse transition.

We observed an increase of the sharpness of the transition with increasing chain stiffness. A double-peak structure in the energy histogram occurred for the stiff chains. The first evidence of the formation of a stable toroidal structure for the stiff-chain globule is also presented.

**STUDY OF MULTIPLIET STRUCTURE FORMED BY TELECHELIC  
MACROMOLECULES IN STRONG AND SUPERSTRONG  
AGGREGATION REGIME: COMPUTER SIMULATION.**

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By means of computer simulation (both molecular dynamics and Monte Carlo) it has been studied the structure of multipliets which are formed in the solution of telechelics, i.e. molecules with strongly attracting end-links.

It was found that in dilute solution in strong aggregation regime such molecules form flower-like multipliets with both end-links entering into one and the same multipliet core. Under equilibrium conditions there are large stable multipliets and gas of unstable micelles with lower value of aggregation numbers. The multipliets are extremely stable and their aggregation numbers  $N_A$  change slightly around average number because of temporary disconnection of one of the ends from core of the multipliet.

The multipliets have dense liquid core formed by attracting ends and diluted coil-like crown created by internal repulsive links. The dependencies of gyration radius  $R_g$  of multipliet core on its aggregation number  $N_A$  calculated for different values of degree of polymerization  $P$  and concentration  $\rho$  of telechelics in the solution were found to be the same and can be approximated as:  $R_g \sim N_A^{1/3}$ .

The aggregation number  $N_A$  of the multipliet decreases with increase of temperature  $T$  and degree of polymerization  $P$  of telechelics chains, and lowering of ratio of interaction parameters  $\varepsilon_A$  between end-links to the interaction parameter  $\varepsilon$  of the internal links.

However, at relatively high concentrations  $\rho$  the morphology of multipliet is changed: the flower-like structure is destroyed, and the bridging between different multipliets is formed by molecules with end-links entering to different multipliets. The structure of arising associative networks was studied as well.

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## COMPUTER SIMULATIONS OF POLYENE OLIGOMERIC CHAINS:

### AN INVESTIGATION OF INTRAMOLECULAR BOND ORDERING

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Polyene oligomeric chains are common and important constituents of biomembrane lipids; biomembranes contain a whole variety of different lipids. Effect of the introduction of double bonds on the orientational properties of lipid hydrocarbon chains is a subject of experimental and theoretical investigations. Defining these properties is a necessary step to gaining a more complete understanding of many important membrane functions, polyunsaturated hydrocarbon chains significance, different lipid microdomain "fluidity". It is the immanent (inherent) properties of different isolated hydrocarbon chains which were thought desirable to elucidate.

A Monte Carlo method has been applied in a calculation of the bond order parameters of unperturbed nonbranched isolated chains with 14 - 24 carbon atoms and 1 - 6 cis double bonds. The molecule-fixed coordinate system with the axes  $\xi_1$ ,  $\xi_2$ ,  $\xi_3$  along inertia tensor eigenvectors of each molecule conformation has been used. The conformations have been generated by a computer, with continuous variation of all single C-C bond rotation angles within the  $(0, 360^\circ)$  range considered, at temperatures 278 - 333 K. The energy of nonbonded interactions, torsion and electrostatic terms have been taken into account. The technique of the importance sampling has been used.

C-H and C-C bond order parameters about the maximum molecule span axis  $\xi_3$  turned out to be decreased from the center of the chain towards the terminals. The order parameter temperature coefficients have been calculated. The magnitudes of cis-monoene chain order parameters of C-H bonds flanking the cis double bond are far less than that obtained for the corresponding saturated chain and significantly differ from one another. The C=C double bond cis order parameter about  $\xi_3$  axis is found to be more high than those of adjacent single bonds. Experimental membrane systems exhibit similar behaviour for the bond order parameters of the bilayer "liquid" range. This has made possible the prognosis of the properties of uninvestigated (experimentally) unsaturated lipids.

The bond skeleton order parameter odd-even effect in the unsaturated chains has been detected. The magnitudes of the order parameters decrease when unsaturation increases. All the C-C and C-H bond distribution functions over the angle deviation from inertia axis  $\xi_3$  have been analysed. This has made possible the statement of the problem of segment fluctuation study of different chemical structure molecules in bilayers.

This work was supported by Russian Foundation for Fundamental Researches (Grant No. 95-03-08199).

## TWO-FLUID MODEL FOR HYDRODYNAMICS OF FLEXIBLE POLYMERS IN DILUTED SOLUTIONS: FURTHER DEVELOPMENT

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At preceding symposium we presented a new model for flexible polymer dynamics [1,2]. This model represents the coil as a droplet of unconnected segment solution held by the external force field. These "entropic" forces tends to establish equilibrium local segment density. The evolution of model is governed by well-known equations of fluid mixture hydrodynamics in external fields. This two-fluid (TF) model is far more simple than the widely used pearl-necklace model and is put forward as an alternative to the porous rigid sphere (PRS) model [3,4]. The TF model offers an advantage over the PRS model in that it accounts the changes of segment densities in a coils due to interactions with flows.

Since in good and  $\theta$ -solvents the segment density is low, the segment diffusion coefficient may be considered as constant and the viscosity of solution may be put equal to that of solvent. In this approximation the TF model involve only one dimensionless parameter, namely, the hydrodynamic interaction parameter, as well as the Gaussian preaveraged pearl-necklace and PRS models.

We have calculated the translational friction coefficient, the intrinsic viscosity and the gyration tensor with TF one - parameter model and compared the results with experiments and predictions of others one - parameter theories. It was concluded that TF one - parameter model is more precise than the FRS model, however they both are useful for cases when only qualitative results are needed.

The ways of the TF model generalization are clearly seen.

This work is supported by Russian Foundation of Basic Researches.

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## SOLVENT FLOW IN NON-DRAINING POLYMER COILS

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Flow of solvent through a polymer coil in diluted solution is treated with a recently introduced two-fluid (TF) model [1,2]. There are two versions of the TF model. The first one involve only one parameter  $P = N\zeta/4\pi\eta_s R_g$ , where  $N$  is the number of segments in a chain,  $\zeta$  is the friction coefficient per segment,  $\eta_s$  is the solvent viscosity and  $R_g$  is the radius of gyration.  $P$  is proportional to the hydrodynamic interaction parameter of the Kirkwood-Riseman pearl-necklace model. The second version takes into account dependencies of the segment diffusion coefficient and the viscosity of segment-solvent mixture, which simulate polymer coil, on local segment density.

It is taken that macromolecule is propelled by an external steady force with the velocity  $v_0$ . When hydrodynamic interaction parameter  $P$  is greater then some threshold value, there is a spherical surface where normal (radial) components of flow velocity vanish. The hydrodynamic interactions range, at which the radius of the sphere  $r_{nd}$  is close to  $R_g$  corresponds to the non-draining regime. The both versions of the TF model lead to equal values of  $r_{nd}$ .

The flows are continuos everywhere and at  $r_{nd}$  in particular. In non-draining regime there are slow circulating flows of solvent at distances from the coil center lower then  $r_{nd}$ . Thus the flow velocities at the coil center cluster in the range  $(-0.1v_0, -0.01v_0)$ .

This work is supported by Russian Foundation of Basic Researches.

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## EFFECTS OF HYDRODYNAMIC-INDUCED COOPERATIVITY ON CONFORMATION TRANSITIONS IN SHORT SIDE-CHAINS

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The hydrodynamic-induced cooperativity plays a decisive part in the dynamics of long polymeric chains, where it leads to a high degree of correlation of transitions among rotational isomers (e.g. [1,2]). It is commonly believed that internal rotations in short side-chains can be considered as independent (or at least the cooperativity is due to potential interactions) since this rotations perturb a medium much less than those of long chains. The goal of this investigation is to evaluate the effects of medium perturbations on conformation transitions rates in short side-chains on a simple model, which makes it possible to distinguish them in "pure" form.

The rates of conformation transitions in the chain of three bonds are calculated for the model when the first bond is fixed and two torsional angles  $\phi_1$  and  $\phi_2$  determine configurations of the chain. It is assumed that viscosity of surrounding medium is high, and Langer's theory, which is a generalization of Kramers' theory to the multidimensional reactions, is employed. It is taken that potential surface has the form  $V(\phi_1, \phi_2) = V(\phi_1) + V(\phi_2)$ , each function  $V(\phi)$  being even and having three minima (*trans*, *gauche*<sup>+</sup> and *gauche*<sup>-</sup> minima). Two centers of viscous friction  $f_1$  and  $f_2$  are assumed to be present at the ends of mobile bonds. The ratio  $\gamma = f_2/f_1$  characterizes the degree of motion cooperativity.

The dependencies of the ratios of the other 8 conformation transitions to that of  $tt \leftrightarrow tg^+$  transition on  $\gamma$  are found. As expected the rate of  $tt \leftrightarrow g^+t$  is less than of  $tt \leftrightarrow tg^+$  transition and diminish as  $\gamma$  increases. An unexpected result is obtained: even in the case of periodical potential, the rate of the  $tg^+ \leftrightarrow tg^-$  transition of the terminal bond is appreciably higher than the rate of  $tt \leftrightarrow tg^+$  transition. Such symmetry breaking is explained by the dependence of the diffusion matrix on the angle  $\phi_2$  and by the twodimensionality of Brownian motion in the saddle region. The symmetry breaking increases with cooperativity parameter  $\gamma$  and disappears in the limit  $\gamma \rightarrow 0$ . For more details see [3].

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# CONFORMATION AND ORIENTATIONAL ORDER OF THE MOLECULS POLYTRIMETHYLSIYLROPYNE IN SOLUTION

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New polymer poly-trimethylsilylpropyne (PTMSP) was synthesized from silicon-containing acetylenes. His hydrodynamic parameters, optical anisotropy and conformation were studied by molecular hydrodynamic and flow birefringence methods.

The Mark-Kuhn-Houwink relationship for the itrinsic viscosity versus molecular weight was established. The flexibility of molecular PTMSP in different solvent was obtained using the hydrodynamic model of a draininng Gaussian coil.

Conformational and optical properties of PTMSP give evidence about the exceeding of the of the double bonds along the main chain and atoms silicium in the side groups in the formation of intramolecuar orientational order.

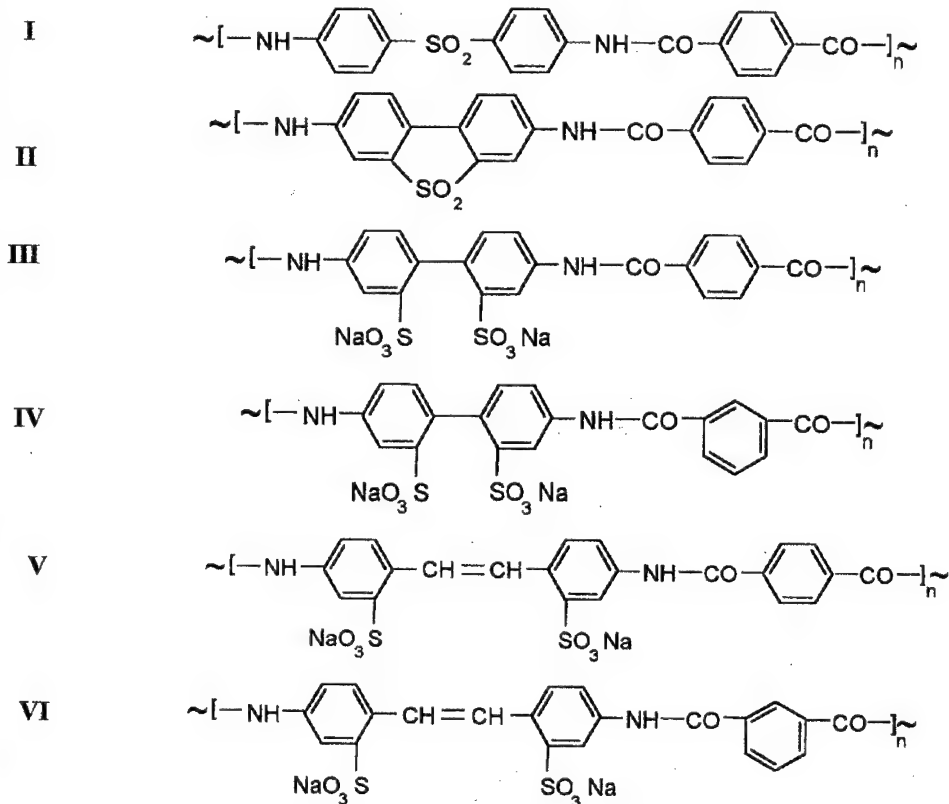
# OPTICAL ANISOTROPY OF THE SULFOXIDE-CONTAINING MACROMOLECULES FROM THE FLOW BIREFRINGENCE DATA

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Optical anisotropy of the macromolecule chain unit is known to be very sensitive to intramolecular ordering of the optically anisotropic groups. Sign and value of the shear optical coefficient is determined mainly by orientation of the main group polarizability axis in relation to the principal axis of the macromolecule. Aiming to determine the intramolecular structure, flow birefringence was measured in dilute solutions in concentrated sulfuric acid for number of the new heterocyclic rigid-chain polymers containing the sulfoxide groups in both main (I,II) and side chains (III-VI).



Experimental data are used to determine the correlation between the structure of the macromolecule repeat unit and optical anisotropy per the chain unit. Conclusions have been made on the space orientation of the sulfoxide groups. Hindrance to intramolecular rotation in the polymer chains and deformation of the backbone are also discussed.

**NON-TRIVIAL STRUCTURE OF POLY(VINYL PYRIDINES)  
FORMED BY ALLYL DERIVATIVES OF CHROMIUM,  
MOLYBDENUM AND TUNGSTEN**

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Allyl derivatives of Cr, Mo and W used as initiators of vinyl pyridines polymerization lead to formation of macromolecules distinguished by very complex architecture.

This is reflected by the composition of these polymers which contain many branching knots and macrocyclic fragments, what follows from the data obtained by mass-spectrometric analysis of the polymers under consideration.

Choice of experimental conditions permits to synthesize polymers with desirable structural and molecular parameters, the latter are estimated by sedimentation-diffusion analysis, light scattering, viscometry.

Poly(vinyl pyridine) chains formed in above cases are of living type, their structure is ruled by the great tendency of the C-metal active bonds to attack the pyridine cycles of polymer chains and create the N-Mt bonds which are also active with respect to the monomer. The many-fold repetition of these acts leads to formation of high molecular weight polymers, up to the  $10^6$  order.

The living poly(vinyl pyridine) chains were used as effective initiators of acrylonitrile and methylmethacrylate. The corresponding hybrid polymers have else more complex structure.

This work was supported by Russian Fundamental Research Foundation (grant N 96-03-33851a).

# COMPARISON OF CONFORMATIONAL PECULIARITIES OF POLY(N-VINYLPYRROLIDONE) SOLUBLE NETWORK STRUCTURES OBTAINED IN DIFFERENT WAYS

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The poly(N-vinylpyrrolidone) (PVP) soluble network structures under investigation were obtained in two ways: 1)  $\gamma$ -irradiation of aqueous solutions of the monomer (N-VP); 2)  $\gamma$ -irradiation of aqueous solutions of the linear PVP macromolecules. The samples were studied by light scattering, velocity sedimentation, translational diffusion, viscometry and GPC.

It is shown that in case of the  $\gamma$ -irradiation of monomer aqueous solution the macromolecules remain linear in the polymerization process up to actually complete monomer working out (way 1). The soluble network structures appear only in 100% conversion region. We considered the detected soluble network structures as macromolecules of complicated architecture formed by several linear macromolecules with their active centres interacting on the complete monomer working out. We supposed that several already formed macromolecular coils (blocks) join into a complex multiblock structure. In order to confirm this supposition we  $\gamma$ -irradiated the aqueous solution of the polymer - the linear PVP macromolecules with  $M_w = 13 \cdot 10^3$  obtained by radical polymerization (way 2). In this case we obtained the same result. Thus, it was shown that the soluble network structures are formed in the process of radiation-induced polymerization of both the monomer and the polymer.

The macromolecular architecture for the soluble network structures of both types depends on the molecular weight of initial linear macromolecules - blocks. As the  $M_w$  values for blocks in the structures of both types differed greatly the structural architecture also had a strong difference. The comparison of molecular characteristics for structures obtained by monomer and polymer irradiation showed that at equal structure molecular weights the soluble network structure is more compact and less soluble in case of a small block than in case of a large one. Thus, we have proved the possibility to control the size of the network cell by varying the molecular weight of initial linear macromolecules (blocks).

This investigation was partly carried out with the financial support of the Russian Foundation for Fundamental Science Studies (project N 96-03-33847a).

# **X RAY STUDIES OF AQUEOUS SOLUTIONS OF POLY(METHACRYLIC)ACID IN THE ABSENCE AND IN THE PRESENCE OF COPPER IONS.**

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Among the polyelectrolytes, the polymethacrylic acid PMA has a particular behaviour since the increase of its ionisation degree induces a conformational transition. Such an effect has an importance consequence on the shape of the curves  $pK_a - f(\alpha)$  which are no more monotonous as in the simple case of PAA (poly(acrylic) acid) but exhibit a minimum and maximum. The position of such minimum and maximum are shifted towards higher  $\alpha$  values when the polymer concentration increase or if salts are added to the solutions. Divalent cations seem to maintain the low  $\alpha$  conformation up to 20 very high  $\alpha$  values.

Despite the great number of works devoted to PMA, the nature of the more compact conformation of PMA before transition has not been elucidated, up to now.

The more recent XRay or Neutron scattering studies deal mainly with the problem of the structure factor which is predicted in several mean field approaches, in the case of weakly charged polyelectrolytes. The comparison between experiments and theory have generally neglected the fact that for PMA, the form factor is not that of a gaussian coil. This introduces some errors on the determination of the structure factor.

We will present a series of experimental investigations performed on a given PMA sample (potentiometric, titration, fluorescence, dynamic and static light scattering, viscosimetry) in pure water, in the presence of monovalents and multivalents counterions.

## DILUTE SOLUTION PROPERTIES OF CARBOXYMETHYL CHITIN

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In the last few years there has been increasing interest in polymers from natural sources. This interest has been driven by the gradual decrease in the amounts of oil as a raw material for synthetic based materials and by the fact that natural polymers are ecologically pure. The polysaccharide *chitin* is one of these polymers. It is the second most abundant natural polymer. Chitin - and its derivatives - have found numerous applications. *Carboxymethylated derivatives* of chitin ("CMCh") for example are of practical interest as matrices for the immobilization of enzymes and other drug substances and as structure-forming and water-retentive components. In the present study, we focus on, the molecular properties and rheology of aqueous solutions of CMCh, and also its film and complex forming properties.

CMCh samples were prepared by alkylation of chitin from crab and krill with monochloroacetic acid in isopropanol in the presence of NaOH. Samples were prepared with 2 degrees of substitution (0.6 and 1.1) with respect to carboxymethyl groups and one degree of substitution (0.80) with respect to acetyl groups. The amount of COOH and NHCOCH<sub>3</sub> groups per polymer chain were calculated from the integral intensity of the absorption bands (C=O) and (amide I) at 1728 and 1640 cm, respectively. CMCh fractions with different molar mass were prepared by fractional precipitation in a water-dioxane system. Both unfractionated and fractionated preparations of CMCh were then investigated by molecular hydrodynamic methods in both unbuffered 0.2M NaCl and NaCl containing phosphate-chloride buffer solution (pH=7.0, I=0.20M) at 25°C. In both these solvents the ionic strength is sufficiently high so that primary polyelectrolyte effects are not significant. Translational diffusion coefficients, intrinsic viscosities, sedimentation coefficients and the concentration dependence coefficients were all measured as well as the refractive index and density increments.

Molar masses of samples and fractions were also estimated on the basis of sedimentation-diffusion analysis: the combination of molar masses with the various translational hydrodynamic characteristics referred to above permits us to establish the corresponding scaling correlations for CMCh, from which molecular conformation and the equilibrium chain rigidity can be estimated. Sizes of CMCh chains were compared to those of previously studied soluble chitin derivatives and other water-soluble polysaccharides. Finally, the effect of increase in ionic strength on these molecular characteristics will be reported.

GMP is grateful to the BBSRC (UK) for financial support during this study.

DYNAMICS OF SEMIRIGID MACROMOLECULES IN  
LONGITUDINAL AND SHEAR FLOWS.

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The object of this study was to investigate the uncoiling process of semidrawing chitozan chains under the elongational flow of semi-dilute water-acetic solutions.

The main method of investigation was the birefringence in the elongational field. The birefringence in the shear flow was also used in order to demonstrate the difference between the influence of elongational and shear hydrodynamic fields at equal rates of the solution deformation.

Experimental data were compared with the predictions of the theory of large-scale chain dynamics. The transition of chitozan macromolecules into the extended state was shown to be a nonequilibrium second-order phase transition. Critical conditions of this transition were determined depending on polymer concentration in the solution and on the ionic strength of the solvent.

The orientationally-deformational influence of this shear field was demonstrated to be significantly weaker than the influence of the elongational field. However, the magnitudes of the deformational relaxation time of the polymer chain as a whole (determined by the two above mentioned birefringence methods) were in a good accordance with each other.

The investigation of the shear and elongational flow of solutions of two incompatible polymers (diacetate cellulose and cyanoethyl cellulose) was also carried out. The gradient dependences of shear and longitudinal viscosity were obtained. Measurements of the longitudinal viscosity of polymer mixture solutions were established to be a more sensitive test of the incompatibility than shear viscosity measurements.

The work was supported by grants: RFFI N 95-03-08614 and HTECH CRG N 940365.



# THE RHEOLOGY OF CHITIN-CELLULOSE MIXTURES AND THE INTERACTION CHITIN-CELLULOSE IN THE COMMON SOLVENT

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The rheology of polysaccharides mixtures in dimethylacetamide with 9% LiCl in range of relations of chitin-cellulose 100:0 at common concentration of polymers in mixtures - 3% was studied. It was shown the abnormal dependence of mixtures dynamic viscosity and  $E_a$  of viscous flow were present at small additions of second polysaccharide. It was established that addition of small quantity of cellulose to chitin solution resulted in an organisation of stronger structure, while the addition of small quantity of chitin to cellulose solution had the opposite effect.

It was demonstrated by method of solvent sorption by films of different composition that the dependence of sorption on composition had abnormal character too.

The parameter of interaction chitin-cellulose had minimal value (negative sign) at range of small addition. It indicates on the compatibility in this system at such composition.

# FORMATION, PROPERTIES AND STRUCTURAL FEATURES OF HIGH-SWELLING ACRYLATE HYDROGELS WITH POLYSACCHARIDES MACROJUNCTIONS.

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Hydrogels are intensively investigated because of their fundamental and practical importance. The application of a new class of crosslinkers - allyl ethers of polysaccharides (AEP) for the synthesis of high-swelling hydrogels has been shown to be efficient in our previous papers. The use of these macrocrosslinkers makes it possible to introduce into networks fragments with definite structure, size and chemical composition and, thus, to obtain gels with different specific structures and properties.

In this study the formation process, the swelling properties and structural features of non-ionic and ionic hydrogels were investigated. The AEP characteristics were varied over a wide range by changing their functionality  $f$  (amount of unsaturated allyl groups), the degree of polymerization  $DP$  and structure (linear or branched). Allyl ethers of dextran, carboxymethyl-, hydroxyethylcellulose and chitosan were used as AEP. The crosslink density ( $n_c$ ) of hydrogels calculated from swelling measurements, as well as the size of microheterogeneities in their network structure obtained by polarized light and small-angle neutron scattering (PLS and SANS) were analyzed as a function of the type,  $f$ ,  $DP$  of AEP and monomer (acrylamide and/or acrylic acid) initial concentration. The values of  $n_c$  and  $n_c^*$  for an ideal network were compared.

These data show that crosslinking centers are formed in the copolymerization of monomer and AEP allyl groups and the efficiency of these reactions is very high. The analysis of  $n_c/n_c^*$  data shows that there are considerable quantities of physical trap entanglements and free chain ends in the network structure of hydrogels.

The results of the evaluation of the microheterogeneities size  $R$  obtained by PLS and SANS were similar. These results suggest that the parameter  $R$  characterizes the dense areas of entangled acrylate chains around the AEP macrojunctions. The factors which can determine the formation of microheterogeneities and their size were discussed. There is evidence of local nematic order of polyelectrolyte chains in the gels, which was observed when they reach the state of equilibrium swelling. This effect can be explained by high values of chains elongation and their tendency to mutual repulsion. In fact, our calculations show that at the maximum swelling the value of chains mean-square end-to-end distance can approach 70% of the contour length.

## THERMOKINETIC PECULARITIES OF GELATINATION CONCENTRATED SOLUTIONS OF METHYLCELLULOSE

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Studies of phase equilibrium, thermodynamic parameters of mixing, kinetics and the rate of mutual dissolution of components is an urgent task for polymer solution science. Furthermore, these data are of a great practical significance since they are necessary to control synthesis and processing of polymers.

Peculiarities of gelatination of methylcellulose (MC) have been investigated in concentrated solutions in water and dimethylacetamide at temperatures from 10° to 80° by vapor solvent sorption. The mechanical properties of MC films were studied using an Instron Testing Machine. The MC films were obtained from solution (I type) or from gel (II type). The sorption of I type films is much higher than the sorption of II type films. The mechanical properties of different type films are also different.

Parts of phase diagrams for MC in overmentioned solutions have been obtained. Flory-Huggins  $\chi$  parameters, Limm-Lundberg's functions of cluster-formation, diffusion coefficients  $D$  of solvent and dependences of  $\chi$  and  $D$  on temperature and concentration have been determined. The activation energy for diffusion and heat of sorption varied depending on conditions of films casting.

The experimental results are compared with the data obtained theoretically using the concept of additivity of group contributions.

We used the simple model of the behavior of MC in systems MC-solvent explaining an interaction of MC with the solvent into two types of films. This model is based on the assumption about the existence of two different types of structural formation involving the solvent molecules.

# **SYNTHESIS OF THREEDIMENSIONAL POLYMER STRUCTURES BY THE REACTION OF CROSS-LINKING OF CELLULOSE AND CELLULOSE ESTERS BY PHOSPHOROUS TRICHLORIDE**

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Reaction of cross-linking of cellulose, diacetate cellulose, hydroxypropylcellulose by phosphorous trichloride ( $\text{PCl}_3$ ) have been investigated in solutions and solid phase. It was established that gelatinous structures were obtained at interaction of cellulose solutions or cellulose ester solutions in organic solvents with  $\text{PCl}_3$ , the velocity of formation of such structures depending on the concentration of the reagents in solution and solvent used, temperature, time factors of reaction.

Structures of products of such interaction of cellulose and cellulose esters with  $\text{PCl}_3$  have been investigated by IR spectroscopy, elemental analysis, pH-titration and sorption. It has been shown that acidic and intermediate cellulose phosphites with different degree of cross-linking were formed at an interaction of hydroxyl group of glucosic group of cellulose and cellulose esters with  $\text{PCl}_3$ ; the composition of cellulose phosphites in final products can be regulated by molar relations of reagents, temperature and time of reaction.

The final structures possess an ion-exchange ability ( $E=1-5 \text{ meq/g}$ ) due to content of acidic cellulose phosphites. They can absorb water and organic liquids with formation of transparent gels. Equilibrium swelling degree in water and organic solvents depend on the degree of cross-linking, chemical structure of esters and rate of phosphorylation. The parameters of crosslinked structures were determined by sorption method.

It can be concluded that materials obtained are prospective in membrane technology and sorption processes since they possess hydrophilic and diphilic properties.

# NMR STUDY OF MOLECULAR WEIGHT DISTRIBUTION IN CROSSLINKED POLYMERS

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Experimental data obtained during the last decades in pulsed NMR polymer studies showed that the transverse magnetization decay contained information on the dynamics and molecular weight distribution of flexible crosslinked polymers. It was shown [1] that, at high temperatures, a free induction decay (FID) for one chain of crosslinked polymer was:

$$G_1(t, \Theta, N) = \exp\left(-\omega_{\text{lok}}^2 (3 \cos^2 \Theta - 1)^2 t^2 \ln N / N^2\right), \quad (1)$$

where  $\Theta$  is the angle between the vector connecting the ends of the chain and magnetic field  $H$ ,  $N$  is the number of statistical segments.

Expression (1) was obtained by taking into account the intrachain dipole-dipole interaction of all the spins of a given polymer chain. For the non-oriented sample,  $\Theta$ -averaging is isotropic,  $N$ -averaging is performed by using the chain-length distribution function  $P(N)$ :

$$G_{\text{intra}}(t) = \int_0^{\pi/2} \int_0^\infty G_1(t, \Theta, N) P(N) \sin \Theta d\Theta dN. \quad (2)$$

Asymptotic estimations of (2) showed that for the chain at the magic angle at  $t \rightarrow \infty$ , FID is proportional to the mean distance  $N_0$  between the nodes of polymer network and inversely proportional to time.

FID has a long slowly decaying component which describes motion of polymer chains with fixed ends at the magic angle to applied magnetic field and is independent of the distribution function  $P(N)$ . The initial portion of FID contains information on  $P(N)$  and varies together with  $P(N)$ .

For high density crosslinked polymer network, the interchain dipole-dipole interaction at high temperature was taken into account. In this case, FID can be given as follows:

$$G(t) = G_{\text{inter}}(t) G_{\text{intra}}(t) = \exp(-\beta t N^{-3/2}) G_{\text{intra}}(t). \quad (3)$$

The expression (3) was derived by using the statistical theory Anderson [2] for magneto-dilute spin systems in suggestion that the nodes are motionless.

From comparison with experimental data, the functions of molecular weight distribution in crosslinked polymers (rubbers, polyurethane, etc.) were obtained.

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## SIDE-GROUP ASSOCIATION IN THE NETWORKS OF COMB-LIKE POLYMERS

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The goal of this work is to investigate the influence of internal and/or external factors on the side group assembling in comb-like polymers, and their networks.

Nuclear magnetic relaxation in chemically cross-linked comb-like polyperfluoroalkyl acrylates PFAA- $n$  ( $n$  is the number of  $\text{CF}_2$  groups in the side group) was studied. The content of the cross-linking agent - allylmethacrylate (AMA) was changed from 0.5 to 5 wt. percent. Using fluorine and proton relaxation data the side-group and main chain mobilities and the local anisotropy of their motion were investigated. The structures of two perfluoroalkyl acrylates ( $n=3, 6$ ) and their networks obtained by the radical polymerization in the bulk state (bPFAA) and by emulsion polymerization (ePFAA) were compared in the present work.

Analysis of the form of transverse magnetization decay shows that with  $n$  increasing from 3 to 6 the structure of networks and of the uncrosslinked ePFAA changes from a homogeneous to a bicomponent one. In opposite, the structure of bPFAA-3 and bPFAA-6 networks and of uncrosslinked polymers is homogeneous. Heating of uncrosslinked ePFAA leads to the homogenization of the structure, while in ePFAA networks cross-linking is shown to stabilize the inhomogeneity. In the bicomponent ePFAA-6 networks there are also two types of the side groups differing in the mobility and in the local anisotropy of motion. In ePFAA-6 networks containing 1 and 2% of AMA the mobility of the rigid fraction of side groups is shown to undergo the abrupt transition at 80-100° C, indicating the disruption of associated states. This process is shown to be reproducible, i.e. the side-group associates are established upon cooling. At lower and higher cross-linking degrees this cooperative transition is suppressed.

The bicomponent nature of ePFAA-6 and its networks is attributed to the core-shell structure of latex particles. Since fluoroalkyl side groups are known to act like surfactants [1], their self-assembling in the shell can be produced by their ordering at the water-particle interface during the emulsion polymerization. The dependence of side groups local ordering on the cross-linking degree is demonstrated and discussed.

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**POSSIBLE MECHANISM OF THE FORMATION OF THE  
SUPERMOLECULAR STRUCTURE IN AROMATIC  
SEMICRYSTALLINE POLYIMIDES EXHIBITING ANOMALOUS  
THERMAL PROPERTIES.**

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The aim of this work is to suggest one of the possible mechanism of the formation of the crystalline structure in polyimides (PI) based on dianhydride with bridged units and on aromatic diamines with meta-attachment and obtained by chemical imidization in solution, in particular in PI based on 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and 3,3'-diaminobenzophenone (DABP) and m-phenylen (DAMP) diamines. These PI exhibit low increment between the glass transition and melting temperatures.

The study of polyamic acid (PAA) BTDA-DABP solutions in solvents of different types by the methods of polarized light scattering in the framework of the Stain statistical theory and proton magnetic relaxation showed that ordered associates are formed from PAA chain fragments in PAA solutions with amide solvents. PI BTDA-DABP and BTDA-DAMP investigations by X-ray scattering and DSC showed that crystallinity appeared only when chemical imidization was carried out in an amide solvent, and in this case the reconstruction of the PI crystalline structure upon exposure to the vapour of amide solutions was in great extent faster in comparison with the case when chemical imidization was carried out in another type solvent.

These results suggest that ordered associates are the "preliminary nuclei" of crystalline structure in PI and their existence may favour a higher growth rate of the crystalline structure of PI during the chemical imidization in solution.

The generalization of results obtained for two PI and the literature data made it possible to propose the indispensable and promoting conditions for the mechanism of formation of metastable supermolecular structure in semicrystalline PI.

## Structure Features of Associative Fluctuation Formations in Polystyrene Toluene Solutions Study by Polarized Light Scattering.

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Some new experimental data on the concentration dependencies of the gyration radii of associated formations  $(R_g)_{ass}$  in polystyrene-toluene solutions are presented. The samples with molecular weights  $M = 0.3 \cdot 10^6, 2.0 \cdot 10^6$  and  $2.8 \cdot 10^6$  are investigated.

The  $(R_g)_{ass}$  values is to be obtained from experimental angle dependencies of isotropic scattering intensity using correlation radii of polarizability fluctuations following by statistic Debye-Bueche-Stein theory.

It is found, that this dependence for solutions of polystyrene in toluene (thermodynamically good solvent) has minimum  $(R_g)_{ass}$  value in the dilute solutions region ( $C[\eta] < 1$ , where  $C$  — concentration,  $[\eta]$  — intrinsic viscosity) and maximum  $(R_g)_{ass}$  in the moderate concentration solutions region ( $C[\eta] > 1$ ).

The character of concentration dependence of max and min values of  $(R_g)_{ass}$  is connected with molecular weights and thermodynamic quality of solution. The PS solution in bad solvent (MEK) yields the independence. Data obtained by the method of dynamic light scattering in polystyrene toluene solution for the sample with  $M = 2.0 \cdot 10^6$  and polymer's concentration  $C = 2.28$  weight % shows the existence of "fast" and "slow" modes for average hydrodynamical radii 80 and 1300 Å accordingly.

Analysis of dynamic characteristics of solutions structure was give by using dynamic light scattering and viscosity data. Data obtained from anisotropy scattering component indicates the reduction of reduced optical anisotropy  $\delta^2/C$  with the concentration growth. The calculation shows that this phenomenon can be explained by the macroform effect.



## SYNTHESIS OF STAR AND LINEAR FULLERENE-CONTAINING POLYMERS AND THEIR BEHAVIOR IN SOLUTION

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Model fullerenecontaining polymers (FP) were synthesized by anionic polymerization using organo-lithium and -potassium compounds including living chains.

Both star and linear polymers with one or two arms (the center of which is fullerene) were obtained on the basis of polystyryllithium. Their behavior in solutions was compared.

Fullerenecontaining polyethylene oxides were obtained by two methods: the formation of active sites on the fullerene molecule as a result of its reaction with an anionic initiator (cumyl potassium or potassium tert-butoxide) with subsequent ethylene oxide polymerization and the grafting of living polyethylene oxide chains on fullerene. Water-soluble fullerenecontaining poly(N-vinylpyrrolidones) (FPVP) were synthesized by free-radical polymerization.

The obtained FP were investigated by the methods of chromatography, light-scattering, diffusion, and ultracentrifugation.

For toluene solutions of star fullerenecontaining polystyrenes the break in the plot of the inverse scattering intensity vs concentration indicates the existence of strong intermolecular interactions including the solvent molecules in solution that retards the fluctuational mobility.

The other example of unusual behavior of the FP in solution is demonstrated by the FPVP. Though, the thermodynamic behavior of the PVP-homopolymer in water and ethanol exhibits no essential difference, the inclusion of about 1% of  $C_{60}$  changes qualitatively the thermodynamics of the FPVP-water system and necessitates the solution to have the micellar structure.

## LIQUID MOLECULES MOBILITY IN RANDOM QUASIPOROUS POLYMER SYSTEMS

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The theoretical and experimental investigations of transport and dynamics for liquid molecules and small particles in random disperse systems of different nature have recently acquired special significance. Besides the obvious "academic" interest, such an investigations are highly important for a variety of technologies: emulsions preparation, gel permeation chromatography, membrane separation and filtration, extraction of oil from porous rocks food and medical industries.

An achievements of experimenters seems to be in many cases much less significant as compared to the progress in the theoretical predictions<sup>1</sup>. The lack of precision experimental information makes it difficult to reveal the retardation mechanisms of saturating liquid molecules mobility in quasi porous random matrices and thus to judge the applicability of existing approaches for describing the small tracers mass transfer and dynamics<sup>2</sup>.

Using neutron transmission and quasi-elastic neutron scattering(QENS) the mass transfer and self-diffusion processes of different liquids in gelatin, PAA and silica gels were studied. It was shown that the macroscopic liquid flow through network of quasi-porous polymer gels at relatively low pressure gradient as well as self-diffusion of solvent and precipitator molecules in the above systems are adequately described by effective medium approach<sup>3,4</sup> with the screening parameter  $k \sim \phi^{0.5}$  or  $k \sim \phi$  which are indicative of a strong influence of hydrodynamic self-interactions or scattering effects on the dynamics of liquids molecules confined by gels pores.

QENS data were also interpreted using the approach which accounts for the hierarchy of time scales of molecular motions in a liquid: slow collective motions of liquid molecules in the content of Lagrange's clusters and rapid single-particle motions. The friction and self-diffusion coefficients data were used to estimate the effective pore sizes  $\xi$  of polymer gels of different concentrations as well as mean sizes of Lagrange's clusters  $R$ .

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## DYNAMIC GLASS TRANSITION OF LIQUIDS IN POROUS MEDIUM

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The static and dynamics properties of confined fluids are of interest in many fields because of their importance in a variety of technological processes including catalysis, chromatography, oil recovery and membrane separations. A considerable amount of progress in understanding the dynamic and thermodynamic properties of molecular liquids in restricted geometry has been made in recent years<sup>1,2</sup>. By studying the glass transition of confined liquids in porous solids, one may obtain not only dynamic but also kinetic information about the confined liquids.

In our work the dynamic processes in liquids of propylene glycol (PG) and two oligomers of polypropylene glycols (PPG) with molecular weights  $M_w \approx 500$  and 1000 g/mol as well as its mixture with ethylene glycol imbibed into the 100 Å pores of controlled porous glass have been investigated as a function of temperature by differential scanning calorimetry.

We find that, in general case, the fluids in the pore are expected to have two distinct phases one of its corresponds to the surface-fluid interface and the other to the inner pore volume. Restricted geometry influences the dynamics through immobilization of some part of PG and PPG molecules at the pore surface and through retardation of the inherent  $\alpha$ -relaxation in the interior pore space. The last effect is most pronounced for the monomer liquid giving rise to maximal increase in glass transition temperature  $\Delta T_g \approx 5$  K. The shift of the glass transition temperature  $\Delta T_g$  gradually diminishes with increasing molecular weight  $M_w$  of PPG that is connected with the less slight ability of its molecules to form branched hydrogen-bonded clusters.

It was shown that after preliminary modification of the glass pores surface by trimethylchlorsilan only one phase of confined fluid in the inner pore volume is observed. The data obtained was revised by existing glass transition theories<sup>3</sup>.

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# THE FORMATION OF IONIC CROSS-LINK NETWORK IN THE PHASE-SEPARATED POLYURETHANE ELASTOMERS

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Polyurethane ionomers have been, and still are, of interest from both the academic and industrial point of view. In segmented polyurethanes it is incompatibility between the hard and soft blocks that results in phase-separated microdomains which, in turn, are responsible for the special properties of these materials. The microdomains act as physical cross-links of a 3-D network.

As a rule, the ionic functionality is incorporated into the hard segment of polyurethane block copolymers. However, the presence of the ionic groups does not allow to obtain the high degree of modification of such polyurethane materials as was the case of the flexible-chain ionomers.

Introduction of ionic functionality into the soft segments of polyurethanes opens up new possibilities for the change of structure-properties relationships. Two series of polyurethanes with carboxylic groups in soft segments have been synthesized. They differ by presence or absence of hard segment units in the polymer chain. Li, Na, K, Zn and Ba salts of these polyurethanes have been prepared. The samples were characterized by calorimetry, wide-angle and small-angle X-rays scattering.

The acidic form of polyurethane without hard segments exhibited an initial one-phase morphology that underwent phase separation upon ionization, with subsequent development of ionic groups ordering and formation of multiplets. The presence of hard segments led to microphase separation with forming of hard-chain microdomains. Upon the introduction of ionic groups into the soft segments of these polyurethanes the microphase separation between ionic and nonionic moieties of the soft segment matrix is observed.

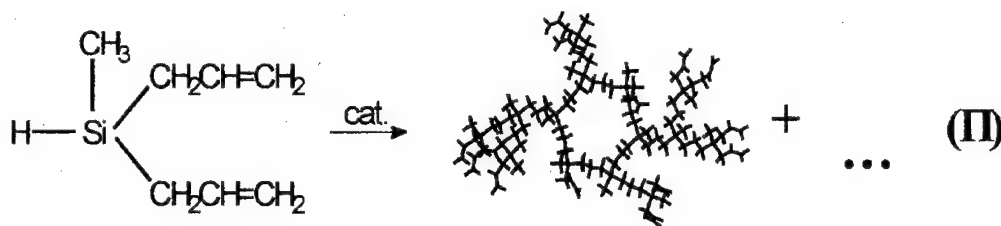
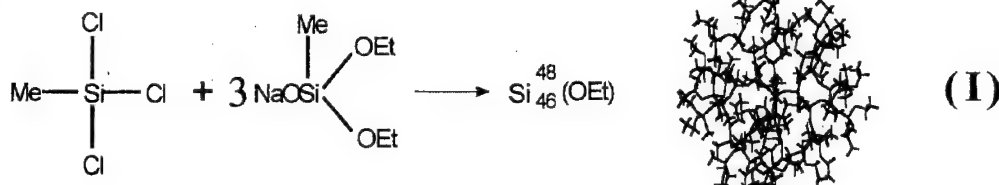
Thus one deals with new polyurethane materials consisting of two types of phase-separated networks. It is shown that these systems combine the properties of segmented polyurethanes on the one hand and of ionomers on the other. Their peculiarities depend on cation type.

## Organosilicon macromolecules of dendritic structure. Molecular modelling and X-ray scattering experiment.

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Molecular mechanics and molecular dynamics computational chemistry methods were applied to study the structure and molecular mobility of novel organosilicon macromolecules of dendritic structure. Two types of macromolecules were investigated: dendrimer  $\text{Si}_{46}^{48}(\text{OEt})$  of regular structure synthesized by multistage method of reiterative growth (I) and "self-organizing" hyperbranched polydisperse system prepared by single-stage synthesis (II).



Autodesk® HyperChem™ rel.3 program (MM+ force field, vacuum) was used on a personal computer with Intel® Pentium® CPU for geometry optimization and annealing simulation.

It was found that optimized and annealed (I) seemed at 300K like a dense uniform ball. The mobility of core fragments at this temperature was rather restricted while the terminal groups on the surface of dendrimer moved very intensively and with high amplitude. Good coincidence was revealed for (I) between calculated shape, size, radial density distribution and experimentally observed by small-angle X-ray scattering technique values.

For (II) the possibility of intramolecular ring formation was studied very thoroughly with the computational methods. Some of the structures were found to be energetically favorable that may be indicative to the existence of a preferable kinetics among very numerous synthetic paths during single-stage synthesis of (II).

This work was supported by Russian Fundamental Research Foundation (grants ## 93-03-18602, 95-03-09376 and Computer Center "FIMIS").

## **Microstructure of polymer system regions with intermediate between crystalline and liquid amorphous ordering**

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A number of mechanisms of the intermediate ordered regions formation were studied for some polymeric systems. The following approaches were applied: (1) the change of the microtactic structure of the small blocks within the polymeric chain (the polyacrylonitrile macromolecule was used as an example); (2) the introduction of the separated fragments with strong mutual interaction inside the polymeric chain (diisocyanate fragments introduced between hard and soft blocks in multiblock copolymers were studied); (3) the creation of a large body of the small blocks with the specific mutual interactions inside the polymeric chain (the chemical modification of the blocks with conjugated bonds in multiblock copolymers of ethylene and acetylene was carried out); (4) the special type of an intramolecular crosslinking (super-crosslinked polystyrene was studied); (5) the special macromolecular architecture (silicon-containing dendrimers were investigated). The systems were undergone to different transformations upon orientation, swelling chemical treatment.

It was found that for the all systems under investigations the upper concentrations of the locally modified fragments within the polymeric chain exist beyond which the pronounced changing in physical and mechanical properties of the whole polymeric system takes place. The approaches (2), (3) and (5) were found to be the most controlled and effective among others mentioned above. These approaches seem to be rather perspective for the further modifications of the real polymeric systems especially of their physical and mechanical properties.

This work was supported by Russian Fundamental Research Foundation (grant # 93-03-18602 and Computer Center "FIMIS").

# INFLUENCE OF CHEMICAL DEFECTS ON THE STRUCTURE AND DYNAMICS OF n-ALKANE CRYSTAL

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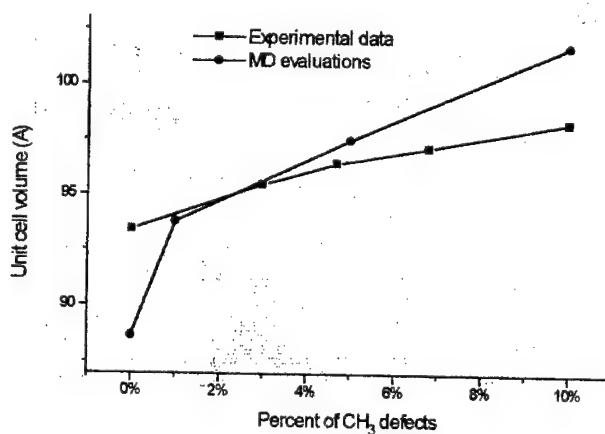
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Computer simulations of the structure and dynamics of n-alkane crystals, both perfect and containing chemical defects (some H-atoms were substituted by  $\text{CH}_3$ -groups) of different concentration, were accomplished. Computational box contained 48 n-alkane chains of  $\text{C}_{50}\text{H}_{102}$ . Periodic boundary conditions were used. Chemical bonds length were fixed and H-atoms considered explicitly. Potential energy of the system included contributions from bending, torsion, and non-bonded Van-der-Waals pair atom interactions.

The temperature and the pressure in the system were kept constant by the use of Berendsen thermostat. Crystallographic parameters of the perfect crystal are well coincide with experimental data. In a wide range of temperatures (200-350K) two different stable crystalline modifications (orthorhombic and monoclinic) were observed. The energy difference between both structures was quite small. In the model crystals the conformational defects have been observed. In particular, the defects  $tg^+tg^-tg^+t$  type were revealed in the orthorhombic crystal

The influence of defects on the structure and dynamics were studied. The Figure shows the changes of volume of unit crystallographic cell due to the concentration of chemical defects that was found from experimental data [Swan P.R. J.Pol.Sci. 1962, v.56, p.406] and from our simulations. The local structure of the chains in the solid state in the closest vicinity of chemical defects are analyzed and discussed.

The work was supported by the Russian Fundamental Researches Foundation.



## WHETHER A FULL LOCALIZATION OF THE SUPERSONIC LATTICE SOLITONS IS POSSIBLE IN THREE-DIMENSIONAL CRYSTALS

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It is well known that non-topological soliton like excitations can exist in one-dimensional anharmonic lattices. The main peculiarities of these nonlinear localized waves are the shape conservation, quasi-elastic collision and the absence of topological charge.

If regarding real three-dimensional lattices, one find that these non-topological solitons correspond to quasi-one-dimensional supersonic plane waves of longitudinal deformation which are localized in the direction of their propagation only. These plane waves may be experimentally observed under very special conditions and do not seem play any important role in the thermodynamics or kinetics of the crystal within usual temperature region.

The question is: whether a complete localisation of one dimensional solitons is possible in three-dimensional lattice? In other terms, if there exist the waves of the solitonic type which do not need the cooperation on the specimen scale in order to propagate without essential dissipation? Positive answer would mean that there exist an additional elementary excitations of rather general type wich may contribute significantly to thermodynamics and kinetics.

The computer simulations disclose that for usual crystals the answer should be negative. The obvious reason is that such excitation have to interact strongly with its vicinity, irradiate energy and disappear quickly.

On the basis of elaborated computer model it is demonstrated that the supersonic soliton-like tensile excitation in the crystallise polyethylene may be manly localized at the single chain. This excitation has considerable lifetime and is charecterised by "acquired topological charge" due to long-range ordering and by discrete velocity spectrum (see Figure).

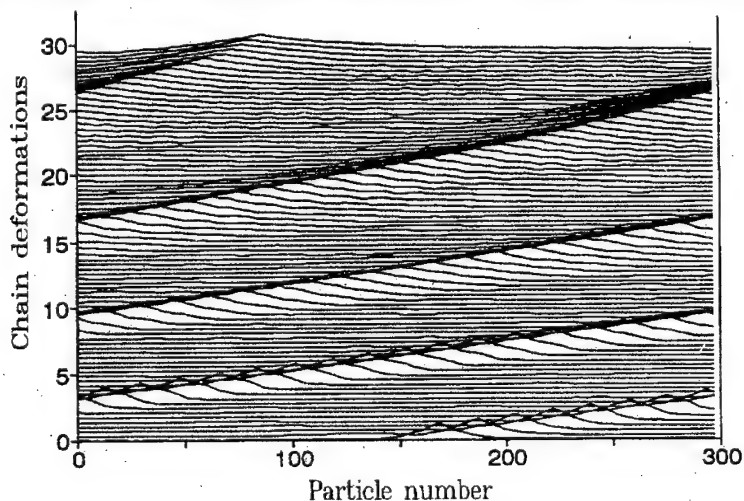


Figure. The soliton in the model of crystal. Chain deformations are plotted with interval 0.15 ps.



## **ABOUT CRITERION OF HYPERBRANCHING FOR POLYMER SYSTEMS**

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Synthesis and property's investigation of hyperbranched polymeric systems are intensively developed last years. Nomenclature and main using terms in this field are not defined exactly. It often leads to contradictories of experimental data interpretations by scientists of different groups. Terms dendrimer, cascade polymer, hyperbranched polymers are widely used, but we cannot now to define exactly degree of structural and phenomenological relations between these types of polymers. Clearly that dendrimers or cascade polymers are the particular case of hyperbranched systems.

On the other hand, precise structural differences between hyperbranched and usual branched polymers are not defined yet from physical point of view.

In this paper we propose logical criterion of hyperbranching. Proposed criterion application illustrated by the data of comparison characteristics of dendrimers and branched polymers the same chemical nature with different concentration of branching centers in the unit of volume. The ability of macromolecules to maintain it's form and size in space can be considered as a criterion. This property is characteristic for dendrimers and hyperbranched polymers. As another interpretation of such criterion the ability of branching macromolecules to form different supramolecular structures may be suggested. The transformation from classic branching polymers to hyperbranching structures takes place at the loss of macromolecule's ability to chain entanglements with increasing of branching center's concentration. So essential transformation of structural peculiarity had to lead corresponding changing of number of characteristics, which can be define immediately, for instance, glass transition temperature, viscosity, diffusion coefficient. In this way, suggested criterion besides determines structural differences of branching polymers will simplify interpretation of experimental results.

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## ASSOCIATION OF AMINO ACID AND PEPTIDE DERIVATIVES OF [60]FULLERENE IN AQUEOUS SOLUTIONS.

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Preparation of new water soluble amino acid and peptide derivatives of [60]fullerene [1] allowed to conduct detailed investigation of their solutions. There were observed the inclination of the molecules, to associate in solutions of different concentration [2]. The extent of association depends on the nature of the amino acid or peptide, namely, on the hydrophilic-hydrophobic balance of the molecule, and can achieve a value of several hundreds of molecules. Besides, the inclination to the association is directly connected with the solubility of the derivatives of [60]fullerene in water.

The most soluble derivatives of dipeptides and arginine (solubility 10-20 g/l) form associates in the region of concentrations of 0,75 to 1,5 g/l. They consist of several molecules, and the number of the latter decreases with the dilution of the solution.

Glycylvaline derivative of [60]fullerene stands out especially. It was highly soluble (20 g/l) and exists as a true solution. The solubility of amino acid derivatives of [60]fullerene is substantially lower and does not exceed 1,5 g/l (glycine-, alanine-, serine-). These solutions with  $c=1,5$  g/l are colloidal. The number of molecules in the associate increases ca. 10 times comparatively with well soluble compounds and reaches several tens and even hundreds of molecules (for the alanine derivative). With the decrease of the concentration of the solution, the associates of alanine and glycine derivatives quickly undergo disassembling. The size of the associates of serine derivative stays constant.

Thus, the hydrophilic-hydrophobic balance of the molecule is responsible for the solubility, extent of association and its dependence on the concentration.

From experimental data, there were calculated diameters of the associates and of individual molecules of the fullerene derivatives. These data correlate well with the computer calculation.

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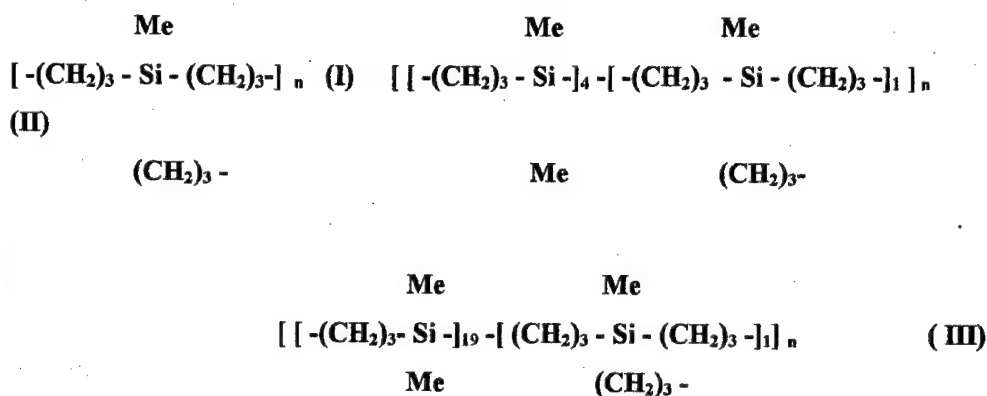
# SUPERBRANCHED POLYMER SYSTEMS. VISCOSITY ANOMALIES OF DILUTED AND CONCENTRATED CARBOSILANE SOLUTIONS

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We investigated solution properties of new homo- and copolymers of carbosilane:



These compounds are superbranched polymer systems. Size exclusion chromatography investigations show that these polymers have wide and practically unimodal molecular weight distributions. Dilute and concentrated solution investigations have shown that dependence of viscosity versus temperature is non-linear. It allowed us to conclude that conformation of the macromolecules is changing during experiments.

# MC-SIMULATION OF CONFINED POLYMERS AT CONSTANT CHEMICAL POTENTIAL USING EXPANDED ENSEMBLE APPROACH

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MC-simulation of polymer and polyelectrolyte solutions confined between two planar walls is considered at thermal and material equilibrium with the bulk while the wall separation is being changed. It corresponds to situations in biosolutions which fill the space between macroparticles or surfaces of the cell components. Of particular interest are internal forces arising in such systems and their dependency on the width of pores. The method used here to keep the chemical potential constant is the Expanded Ensemble approach [1] which is based on simulating the system at a number of slit widths simultaneously. The chemical potential itself is not calculated (hence there is no need to insert/delete particles) but it can be determined for any simulated subsystem separately.

The idea of the Expanded Ensemble method [1] is combined with the isotension ensemble approach for simulation of solutions in slits [2]. The additional variable for expanded isotension ensemble is  $h$  - the width of the slit. Extended random walk in the space of  $h$  ( $h_1, \dots, h_M$ ,  $M$  appr. 10) and application of an appropriate iterative procedure for equalizing the relevant probabilities enable us to make the chemical potential equal for all values of  $h$ .

Most calculations were carried out for systems consisting of non-charged polymers. Independently varying their length ( $N = 4, 8$  and  $15$ ) and the volume fraction ( $0.0025, 0.036, 0.045$  and  $0.063$ ) we obtained results which agree with an experimental fact that depletion attraction appears between the surfaces confining macromolecules of a chain length long enough. The dependencies of the solution density and both osmotic and lateral pressures on the wall separation show that the system is very close to the bulk conditions for wide slits. For one of the system considered ( $N = 15$ ) a MC run was performed with positively charged monomers and the same number of negative counterions. Comparison of the two results proves that the coulomb interactions considerably decrease the depletion attraction effect making all the dependencies much weaker.

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## KINETIC OF THE PHASE TRANSITIONS IN POLYACRYLONITRILE / PROPYLENE CARBONATE SYSTEM

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Polyacrylonitrile (PAN) / Propylene Carbonate (PC) system is of interest owing to ability to form polymer monocystal or thermoreversable gel.

In present paper we report the results of studies of the phase transition kinetic determined morphology of resulting phase in high molecular mass PAN ( $M_n = 2.0 \times 10^6$ ) / PC system. The main physical method was turbidimetry carried out with the set specially developed for this aim on base UV-spectrometer SPECORD - 40. The initial gel was prepared by the following manner. Swollen at 20°C in PC polymerization powder (polymer concentration - 1÷5 wt.%) was heated up to 140°. This temperature corresponds to formation homogeneous solution. After then the solution was cooled up to 20°C and gelated at the temperature for 24 hour.

The various ways of thermotreatment of PAN / PC system were analyzed:

- continuous heating and cooling with constant rate (ab. 4°/min);
- thermotreatment under constant temperature of the samples coming to this condition from higher and lower temperature;
- melting of the various manner thermotreated gel samples.

As a results kinetic characteristics of gel melting and solution gelation was found. It was shown that the width of melt interval depends not only on heating condition but also on nonuniformity of the gel structure. Thermotreatment at the same temperature of gels coming from higher and lower temperature results in inequivalent affects. The polymer concentration in solution in high degree influences on gelation rate increasing the letter by 10 times under increasing the former from 1 to 5 wt.%. and does not practically influence on maximum gelation rate temperature.

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## DENSITY OF TOPOLOGICAL RESTRICTIONS IN POLYMER NETWORKS AS PREDICTED BY THE THEORY OF RUBBER-LIKE ELASTICITY

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The topological restrictions (TR) in polymer networks which are connected with the impossibility of mutual chain crossing leads to a considerable limitation in the mobility of the latter. TR stipulate two effects which are not considered in the classic theory. These are: a) the infringement of deformations affinity of individual chain parts and b) the change of chains fluctuation limitation in the direction normal to the "channel" contour. The existing theories of rubber-like elasticity which are based on the concept of TR take into account, as a rule, only one of these effects.

A theory of rubber-like elasticity that considers simultaneously both sides of TR influence on elastic properties of polymer networks is proposed. According to this theory the expression for stress at one-dimensional deformation has the form:

$$f = 2C_1(\lambda - 1/\lambda^2) + C_2 \Phi(\lambda, \beta)$$

where  $C_1$  and  $C_2$  are constants,  $\lambda$  - extention ratio and  $\beta$  is ratio of mean square chain fluctuation in the direction normal to the "channel" contour in undeformed state -  $\langle h^2 \rangle$  to the mean 2 square of chain length in a free state -  $Nl^2$ . A good agreement with experiment is observed when values of  $\beta$  are equal to several hundreds. If the primes of the theory are correct it means that chain fluctuations in real polymer networks are limited in a great degree and the chain mean square deviation from the "channel" contour (the middle position of the chain) -  $\sqrt{\langle h^2 \rangle}$  is less than the distance between cross-links in the network-  $\sqrt{Nl^2}$  approximately by ten times.

## PHYSICOCHEMICAL CHARACTERISTICS OF PDMS-URETHANE PREPOLYMERS

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Film-forming PDMS-Urethane (PSU) prepolymers were synthesised from hydroxyalkyl - terminated siloxane oligomers and tetramethylxylenediisocyanate and their physicochemical characteristics were determined. Each sample was a viscous liquid.

Several techniques (SLS, DLS, FTIR, SEC) were applied to determine the structural parameters of PSU in toluene solutions, whereas some other techniques (optical microscopy and again FTIR) were used to investigate their structure with no solvent applied.

The molecular weight ( $M_w$ ) of PSU samples ranged from 10,000 to 100,000 g mol<sup>-1</sup>.

Microgels were found by the SLS method to occur in toluene solutions of some specimens. The Lange procedure enabled the molecular parameters to be determined for molecularly dissolved prepolymers and for microgels.

The hydrodynamic dimensions ( $R_H$ ) estimated by DLS are comparable to those of the structures observed under the optical microscope, i.e., about 100 nm and more.

The optical microscopy method allowed to detect ordered or crystalline structures in most PSU samples.

The FTIR analysis used to study the chemical structure of PSU samples showed the contents of NCO, NH and C=O groups to vary with time.

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## Diffusion of Polystyrene Spheres in Hydroxypropyl Cellulose Solutions

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Self diffusion coefficient of polystyrene (PS) spheres suspended in hydroxypropyl cellulose (HPC) solutions was studied by the dynamic light scattering technique. HPC chains tend to adhere to the PS surface, and in the case of a small sphere and long chain length, the sphere may be thought of as a bridge linking many chains. When a nonionic surfactant, Triton-X, is added, the interaction between HPC and the polystyrene spheres is reduced. We compared and studied diffusion coefficients of polystyrene spheres as a function of Triton-X concentration or the interaction strength. Three polystyrene sizes and three HPC molecular weights were used to study their effects on the interaction strength. The dependence of polystyrene sphere diffusion coefficient on HPC concentration can be easily altered by adding the surfactant, confirming that without the surfactant the polymer chains bind to the sphere surface. Bare polystyrene spheres diffuse more rapidly through HPC solutions than the sphere-polymer complexes, because of the additional hydrodynamic drag force. Two diffusion regimes will be identified and compared: dilute and semidilute HPC concentration regimes.



## IR SPECTROSCOPY OF THE POLYMER GELS

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Discovering the structure of polymer gels is very important in connection with the problem of obtaining high strength fibres (gel-technology), creating high porosity sorpting and highly effective filtrating materials, their using for transportation of the medicinal preparations, etc. [1].

We have suggested comfortable and informative IR spectroscopy technique to study the polymer gels [1 - 3], which made it possible to judge about the nature of gel network junctions, the character of gel-forming and many others.

The gels obtained out of three high molecular weight polymers (PE, PAN, PVA) used in order to receive of high strength fibres have been studied in the current article. Gels were obtained through the cooling PE-decalin or PE-*p*-xylene, PAN-DMA/water, PVA-water of solutions. In IR spectra of gels were selected the regions, which are free out of solvent influence. ATR-technique was used to study IR spectra of the thick films of gels. IR spectra of gels were investigated in dependence on the polymer molecular weight, the polymer concentration in solution and the temperature of the experiment. It was found, that in all cases the junctions of physicall gel network have the crystalline nature. IR spectroscopy method was worked out for the purposes of the degree gels crystallinity and the porosity PE xerogels evaluation. The mechanism of PE gels shrinkage, accompanied by wring of the solvent and associated with crystallization processes was also investigated.

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# PECULIARITIES OF SEGMENTAL DYNAMICS IN AMORPHOUS POLYMER BLENDS AS A CONSEQUENCE OF THE COMMON NATURE OF $\alpha$ AND $\beta$ RELAXATIONS

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Segmental dynamics in two series of polystyrene - poly( $\alpha$ -methyl styrene) and polystyrene - poly(vinyl methyl ether) miscible blends has been studied in detail by DSC. A number of dynamics characteristics, including the temperature dependences of motional activation energies over the range from  $\beta$  relaxation region to  $T_g$ , the scale of motional unit event and the values of intermolecular cooperativity degree  $Z$  for segmental motion, have been determined.

The complicated  $T_g$  versus composition relations, sharply reduced values of  $T_g$ s, glass transition activation energies and motional event scale as well as the multiply broadened transition ranges in blends have been observed. At the limit, parameter  $Z$  decreased from 3-4 to 1 and, for the first time, the linear activation energy versus parameter  $Z$  relation for segmental motion has been found experimentally. Two kinds of segmental dynamics heterogeneity at  $T_g$ s in single - phase blends have been shown, viz.

(a) manifestation of two glass transitions shifted, judging by their characteristics, down to  $\beta$  relaxations for blend components, and (b) the wide (by 2.5 times) activation energy dispersions, corresponding to both non - cooperative and cooperative segmental motions, within a single broad glass transition range.

All the effects observed could be interpreted and predicted, to some extent quantitatively, proceeding from the conception of the common segmental nature and interrelationship of  $\alpha$  and  $\beta$  relaxations, as a consequence of partial or complete breakdown of intermolecular cooperativity of segmental motions.

## PHENOMENOLOGICAL DEPENDENCES OF SEVERAL PHYSICAL PROPERTIES OF POLYMERS ON THEIR CONFORMATIONAL RIGIDITY.

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Phenomenological dependencies of several physical properties such as the softening temperatures, friction coefficients, elasticity modulus, fire-resistance parameters and quantum luminescence yield on the conformational rigidity of the polymeric chain are found for aromatic and heterochain polymers. This class of polymers appeared to be the most appropriate object for investigating the conformational characteristics. The absence of hindered rotation predicted by quantum-chemical calculations [1,2] and confirmed in our works [3-6] allowed us to find conformational parameters avoiding time consuming calculations of the conformation energy maps.

We have shown that various physical properties of polyheteroarylenes, which depend on numerous factors, first of all such as intermolecular interactions, appeared to be dependent on the conformational rigidity of the polymer chain. The conformational rigidity of the polymeric chain determines the capability of the chain elements to move in space due to feasible conformational transitions, i.e. it directly determines the chain mobility upon heating (softening temperature), in the friction processes, upon stretching of the specimen or in testing its yield strength. The conformational rigidity of the polymer chain is not immediate in the combustion and luminescence processes. In the first process it affects the softening temperatures on the specimen surface and the diffusion rates of several chain fragments to the combustion surface; then, the more is the freedom of motion of the chain elements, the faster are the combustion processes. In the case of luminescence, the higher is the conformational flexibility of the polymer, the easier is the transformation of energy into the thermal motion of the polymer chain elements and the lower is the radiation emission.

Such dependencies of physical properties of polymers on the conformational rigidity of the polymer chain provide new opportunities for the molecular design of polyheteroarylenes to synthetic chemists. If the conformational characteristics of these polymers are considered together with cohesion energies, the predictive power of the available method becomes significantly greater.

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# ON-LINE DETERMINATION OF POISSON'S RATIO OF HDPE FILMS BY SPECKLE PHOTOGRAPHY\*

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Double exposure speckle photography, DESP, has found this far a few applications in the field of oriented polymers although it is among the few methods that allow on-line determination of micro-displacement. It is based on speckles usually observable in scattering patterns of polymers when recorded in coherent light which arise because of interparticle interferences x1!. The conventional (in strain analysis) DESP technique was first extended to polymers for determination of Poisson's ratio during deformation of extruded polyolefins x2!.

In this paper, DESP analysis is applied to tubular films of high density polyethylene which were stretched at room temperature and low strain rate. The DESP patterns were on-line recorded on drawing the films along and across the extrusion direction. The relative extension in length and contraction in width during heterogenous deformation were measured by taking point-by-point diffraction at DESP patterns. Local values of the apparent Poisson's ratio of strained specimens exceeding 0.5 were obtained with both regimes of stretching even at the early stages of 4-5 %. The results were considered in the light of previous measurements on HDPE and discussed in terms of structural mechanics.

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# THE BEHAVIOR OF THE MACROMOLECULES TERPOLYMER ON THE BASIS OF STYRENE IN DILUTED SOLUTIONS.

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The heterogeneity of the composition and chain length of the three component copolymers of styrene with acrylonitrile and methyl methacrylate obtained at concentrations change of each component in limits 5-95 mol.% and constant relationship of two other monomers 1:1 were studied by methods of  $^1\text{H}$ ,  $^{13}\text{C}$  NMR-, IR-spectroscopy, light scattering, GPC and viscometry. Analysis of triad sequence distributions with central units of styrene acrylonitrile ( $^{13}\text{C}$  NMR) and methyl methacrylate ( $^1\text{H}$ ,  $^{13}\text{C}$  NMR) showed that their common content accounts for on the average 48 wt.%. Degree of copolymers composition heterogeneity is equal to 28 wt.% from maximal one for interval of approximate azeotrope compositions and 57-62 wt.% beyond of it. Component contribution in unperturbed dimensions of macromolecular coil are practically additive at acrylonitril units component in the chain lower than 44 mol.%. Correlation of parameters of short- range and long- range order interaction, unperturbed chain dimension, steric factor of braking internal rotation and swelling degree of macromolecule coil with copolymer composition and unit sequence along chain is established. Equations for calculation of molecular weight and MWD of three component copolymers according to their composition data, GPC-chromatograms and the limiting viscosity number measured in GPC-solvent have been proposed.

## DNA Interaction With Metal Ions and Complexes of Pt(II)

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The comparison studies of the hydrodynamic and optical properties of DNA during its interaction with mono-, di- and trivalent counterions have been done. It was shown that the persistence length of DNA is a rather conservative parameter. It doesn't depend on the charge and concentration of counterions in a wide range of ionic strengths  $\mu > 0,002M$ . The polyelectrolyte expansion of DNA depends on ions valence, but has only a weak dependence on their bonding positions. At  $\mu > 1M$  the effective volume of DNA doesn't depend on the nature and concentration of mono- and divalent ions as a result of suppressing of the polyelectrolyte expansion. At  $\mu > 2,4M$  NaCl the sharp increase of the DNA optical anisotropy was observed. The bonding of trivalent ions  $Fe^{3+}$  to DNA leads to its compactization independent of the ionic strength of the supporting electrolyte. Compactization is accompanied by the appearing of mutually oriented DNA parts ensure the increase in the optical anisotropy of DNA. The interaction of DNA molecule with some coordination compounds of Pt(II) has been studied. It was shown that the transition of the cis-DDP, trans-DDP and other non dissociated compounds to their charged aqua-complexes is necessary for their binding to DNA in solution.

## **A New Model of Radiation-Induced Damage of DNA Molecule.**

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The results of hydrodynamical and optical investigations of DNA molecule  $\gamma$ -irradiated in aqueous-salt solutions allow us to conclude that conformational changes of macromolecule, observed at doses 10–20 Gy, are caused by additional screening of charge of macromolecule. In this work the role of solvent structure in the process of the irradiation is proposed to be elucidated.

It is known, that the aliphatic alcohols stabilize the structure of water in wide range of their concentrations in aqueous-alcohol solutions. At the so-called 'critical' concentration alcohol destroys the spatial structure of water. In this connection the changes of the long-range and short-range interactions of the DNA molecule  $\gamma$ -irradiated with doses 10 Gy in aqueous-ethanol mixtures of different ethanol and counterions content were studied. In experiments it has been turned out that the radiation-induced conformational changes of the DNA molecule decrease along with the increase of the stabilization of water structure and at certain concentration of ethanol, which depends on ionic strength, these changes disappear. At the critical ethanol concentration the radiation-induced conformational changes of the DNA molecule are the same as the conformational changes of the DNA, irradiated in aqueous-salt solvent. Investigations of these systems, irradiated at doses 20 Gy, have revealed that in the interval of alcohol concentrations when the structure of water is stabilized, the behavior of measured parameters is qualitatively the same as that in the systems, irradiated at the dose 10 Gy. It has been found that there is qualitative difference between the studied parameters of the DNA molecules, irradiated at doses 10–20 Gy, at ethanol concentrations higher than the critical one.

The interpretation of the obtained results is presented in the report.

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## ORDERED LIQUID-CRYSTALLINE EPOXY NETWORKS

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The lecture reveals the influence of molecular ordering on the cure kinetics of epoxies and the effect of network formation on the orientation of polymer formed in the magnetic field.

It was shown that there are no difference in reactivity of liquid-crystalline diglycidyl ether of terephthaloyl-bis(4-hydroxy benzoic acid) (DGET) in the nematic and isotropic state. The effect of magnetic field on the DGET cure kinetics in liquid-crystalline phase was studied using calorimetry, NMR, and X-ray diffraction. The magnetic field was shown to inhibit DGET anionic polymerization under the action of tertiary amine.

The ordering parameter of polymer in the course of DGET thermal self -cure decreases to the ultimate value of 0.5, whereas in anionic polymerization, virtually complete disordering is attained. The ordering of network polymer can be preserved if the polymerization of DGET is performed according to a programmed temperature history.

The reasons of revealed phenomena are discussed.



## MODEL OF PHYSICAL NETWORK FOR POLYMER CHAIN RELAXATION PROCESS

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Concept of physical networks is used generally for polymer systems in which intermolecular interactions are localized. Some results in this fields were obtained in works [1-4]. We have shown the possibilities of the concept of physical networks to describe the relaxation properties of any polymer systems [5]. Our consideration is based on two main ideas.

The first one is: chain conformations in condensed systems are supposed to be expressed through a set of equilibrium and nonequilibrium physical crosslinks.

The total quantity of the physical bonds per chain depends on the system state (temperature, polymer concentration, chemical structure) and does not depend on deformation. The deformation effect on the chain conformation can be displayed via relation of equilibrium and nonequilibrium bonds.

The second one consists in the possibility to consider and to describe relaxation process as transformation of nonequilibrium bonds to equilibrium ones.

The definition of the nonequilibrium crosslinks is the follow: conformation of the interchain between them is nonequilibrium; for Gaussian model it means that average interchain dimension  $\langle r^2 \rangle \neq n \cdot l^2$  ( $n$  and  $l$  are the segment number and length, accordingly). In the simplest case we can consider kinetics of nonequilibrium crosslinks  $x$  as:

$$dx/dt = -x/\tau$$

with initial conditions:  $x=x_0$  at  $t=0$ . It is obviously the concentration of physical crosslinks  $x_0$  depends on system state and is proportional to polymerization degree of the polymer chain.

As far as the physical crosslinks are connected with the chain it leads to dependence of  $\tau$  on the chain conformation; therefore,  $\tau = f(x)$ . The results of computer simulation experiments are presented in the work. It was shown  $\tau = \tau_0 x^\alpha$  where  $\alpha \gg 1$ ;  $\tau_0$  is the function of the system state (temperature and concentration) only. Taking into account this result solution of eq.(1) leads to:

$$x = x_0 - (t/\theta)^{1/\alpha}, \quad (2)$$

where  $\theta = \tau_0 x_0^{1/\alpha}$

The view of the eq.(2) is such that for high values of  $\alpha$  the curves  $x(t)$  can be approximated by stepwise function  $u(t)$ :

$$u(t) = x/x_0 = 1 \text{ at } t < \theta \text{ and } 0 \text{ at } t \geq \theta$$

So, in the first approximation, the relaxation proceeds as stepwise process: there is no relaxation at  $t < \theta$  and then relaxation occurs. This relation results, as it is shown in the work, that the form of temperature or time dependencies of relaxation modulus is connected with polymer MMD. So, there are possibilities to obtain data on molar mass distribution from relaxation spectrum of linear [51 and crosslinked polymers. They arise due to using model of physical networks.

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## SOLID-LIQUID PHASE SEPARATION CAUSED BY MECHANICAL FIELD IN POLYMER SYSTEMS

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The solid-liquid phase separation of the polymer solutions and blends: polyethylene-PE ( $\overline{M}_n = 2.3 \cdot 10^5$ ) -p-xylol, polypropylene glycol-PPG ( $\overline{M}_n = 3100$ )-polyethylene glycol-PEG ( $\overline{M}_n = 800$ ), polyvinylacetate-PVA ( $\overline{M}_n = 1 \cdot 10^5$ )-polyethylene oxide-PEO ( $\overline{M}_n = 2 \cdot 10^4$ ) were studied under shear field and in static conditions using the cloud point, light scattering and viscometric methods. The phase state of polymers was studied using X-ray analyses and polarizing microscopy.

It was discovered that the mechanical action leads to the dramatical increase in crystallization temperatures of PE, PEG, PEO. This phenomenon is caused by the orientation of macromolecules in shear flow. The orientation entropy is calculated.

It was shown that the influence of shear field on the values of phase separation temperatures has an extremal character depending on polymer concentration and shear stress.

It was discovered that the mechanical field leads to the change of the boundary curve shape. It may be caused by the change of phase separation mechanism of the systems.

# AGGREGATION OF DISPERSED PARTICLES INTERACTING WITH POLYMER CHAINS: THE INTEGRAL RISM EQUATION THEORY

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A microscopic theory of binary systems of the type "macromolecules + dispersed particles" is developed on the basis of the reference interaction site model (RISM) integral equation technique. The obtained general equations allow one to calculate the correlation functions and thermodynamic characteristics of the system at an arbitrary ratio of the components. The developed theory is employed for a comprehensive study of interaction of small spherical particles with polymer chains in the regimes of weak and strong adsorption of the macromolecules on the surface of the particles. The temperature and concentration regions characterized by different effect of the polymer on stability of the dispersed component are determined. The aggregation of the particles in a polymer matrix is studied. In this case the central object in our studies is the so-called connectedness pair correlation function,  $h_{\alpha\beta}^+(\vec{r}, \vec{r}')$ , giving the probability density that particle  $\alpha$  exists at position  $\vec{r}$  and particle  $\beta$  in the same cluster exists at position  $\vec{r}'$ . The mean cluster (aggregate) size  $S$  is given by  $S=1+\rho\lim_{q\rightarrow 0}\hat{h}_{\alpha\beta}^+(q)$ , where  $\hat{h}_{\alpha\beta}^+(q)$  denotes the spatial Fourier transform of  $h_{\alpha\beta}^+(\vec{r}, \vec{r}')$  and  $\rho$  is the number density of particles.

It is shown that at higher density of one of the components of the binary athermal system (i.e., at higher density of the medium) aggregation of the second component (i.e., dispersed particles) is more intensive. With the chain length  $N$  increasing, the effect of the polymer environment on the aggregation of the particles is diminished; however, at sufficiently large  $N\sim 10^3$  the asymptotic regime is achieved, where the role of the parameter  $N$  is insignificant. In the case when polymer segments are adsorbed on the particles, with temperature decreasing the average aggregate sizes  $S$  first decrease and then begin to grow. A simple model is suggested to explain such nonmonotonic behavior. The conditions for the critical region of the parameters (temperature and polymer density), in which a macroscopic cluster is formed (in other words, condensation of particles occurs, which is induced by adsorption of macromolecules), are obtained.

The authors are grateful to the *Russian Foundation for Fundamental Research* for financial support. P.G.K. and A.R.K. also gratefully acknowledge the support of the *E.I.DuPont de Nemours Company* (in the framework of agreement *Novel Polymeric Systems*).

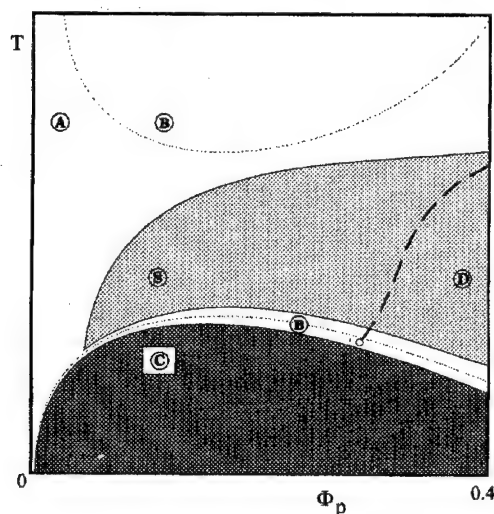
# INTERACTION OF DISPERSED PARTICLES WITH MACROMOLECULES: ANALYSIS OF THE INTEGRAL RISM EQUATIONS

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A detailed study of interaction of small spherical particles with polymer chains in the regimes of strong and weak adsorption of macromolecules on the surface of the particles is performed on the basis of the integral RISM equation theory. The temperature and concentration regions characterized by different effect of the polymer on the stability of the dispersed component are determined. The conditions of formation of thermodynamically stable quasiregular structures are established. The corresponding temperature - concentration state diagrams are constructed. We summarize the results of calculations in Fig.1, which gives a schematic representation of the complete state diagram of the system in the temperature ( $T$ ) - polymer volume fraction ( $\Phi_p$ ) coordinates (density of particles,  $\rho_d$ , is assumed to be fixed).



The dotted lines in the diagram are the curves of quasiideal behavior of the dispersed component. In these curves the reduced compressibility of particles  $\chi$  is the same as of the ideal gas ( $\chi=1$ ). In the region A, which lies between the upper and lower curves of quasiideal behavior, we have  $\chi < 1$ . In two regions B that lie above the upper curve and below the lower curve we have  $\chi > 1$ . In the subregion S, which is a constituent of the region A, the conditions of the increased stability of dispersion are realized. In this region compressibility is considerably lower, as compared to the system of individual particles at the same density, i.e., stable adsorption complexes are formed because of linking together

chains and particles. On the boundaries of the region S the polymer additives do not affect compressibility of the dispersed component. In the region C intensive aggregation of particles occurs. This is due to their effective attraction increased by strong adsorption of chains. In this case a singularity of  $\chi$  is observed ( $\chi \rightarrow \infty$ ). The dashed line that begins at the boundary of the subregion C defines the region D, where packing of stable adsorption complexes results in formation of quasiregular structures with periodic alternating of particles and polymer segments. Note that the state diagram presented in Fig.1 corresponds to a dilute and semidilute polymer solution and does not describe the behavior of the system at higher concentrations of the polymer.

The authors are grateful to the Russian Foundation for Fundamental Research for financial support. P.G.K. and A.R.K. also gratefully acknowledge the support of the E.I.DuPont de Nemours Company (in the framework of agreement Novel Polymeric Systems).

## STRUCTURE OF A COLLAPSED POLYMER BRUSH UNDER DEFORMATION

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We present a theoretical study of the equilibrium structure and properties of a planar brush under poor solvent condition, and the way it responds to normal deformation (stretching or compression). First, for a non-deformed brush it is shown that at moderate grafting density, the chains form micelle-like aggregates with globular cores and extended legs pinned to the surface at the grafting sites. The driving force for the micelle formation is due to the surface free energy which can be minimized by forming droplets (micelle cores) at the expense of stretching relatively small parts of the chains to produce legs. The micelles are stable in a wide range of grafting densities provided the chains are long enough and the solvent is poor so that  $|\tau|N^{1/2} \gg 1$ . We analyze various scaling regimes corresponding to homogeneous collapsed brush, pinned micelles, and isolated grafted globules, and construct the complete diagram of states.

Under normal deformation, stability of the pinned micelle regime changes and so do the equilibrium micelle parameters (aggregation number, free energy, etc.) In the process of a quasi-equilibrium deformation, a brush will undergo a structural rearrangement that will determine its elastic response. Compression leads to a decrease in the aggregation number, and generally favors either a completely homogeneous structure or a system of isolated compressed globules. Conversely, stretching increases the aggregation number and promotes pinned micelle stability. For a given brush (grafting density and chain length being fixed), stretching will result in a laterally inhomogeneous structure even if one starts from a homogeneous brush. Various scenarios of brush deformation are predicted depending on the state of the non-deformed brush. Most of them involve a crossover from one scaling regime for the elastic response to another. Strong hysteresis effects in the interaction of two collapsed brushes once they are brought close to each other and then separated again are discussed.

# Theory of Polymer Brushes of Liquid-Crystalline Polymer

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March 6, 1996

The liquid crystalline ordering in polymer brushes formed by macromolecules with mesogenic groups in main chain and immersed in a solvent is investigated theoretically. The numerical method of self-consistent field approximation was used.

Two phenomena connected with the phase nature of this order-disorder transition are found:

The existence of the microphase segregated brush regime is shown. The intrinsic sublayer shows up as a collapsed orientationally ordered brush. It is separated from the external swollen sublayer by an interphase boundary.

At high grafting density ( $\sigma$ ) the transition from the common brush regime to microphase segregated form is continual. At small  $\sigma$  it is jump-like first order phase transition for a finite chain length ( $N$ ), but the value of this jump tends to go to zero for the limit  $N \rightarrow \infty$ .

## **Liquid-crystalline ordering in polymer brushes with restricted segments mobility**

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The mean-field theory of liquid-crystalline (LC) ordering is developed for a polymer brush immersed in a solvent. Additional attraction between neighbouring parallel mesogenic segments of the grafted chains is taken into account. Following models are under consideration: 6-choice and 5-choice cubic lattice models; 5-choice cubic lattice model with trans-gauche isomerism; cubic lattice model with normal deformations. It is shown that LC ordering is connected with the loss of solubility and occurs as a discrete first-order phase transition which is similar or even identical to transition in polymer solution. There is also a phase-like transition for isomers distribution.

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## Computer simulation of polymer brushes under the shear deformation

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The structure and dynamics of two interacting polymer brushes grafted on two parallel planes with and without shear deformation were investigated by the methods of Brownian dynamics (BD) and stochastic dynamics (SD). Some calculations (without shear) were performed also by molecular dynamics (MD) method. System consisting of  $M$  chains with two dimensional periodical boundary conditions and rigid unpenetrable planes in third direction was studied. Chain consists of  $N$  segments which interact with each other, with segments of other chains and with planes by means of Lenard-Jones potential. The number of chain ( $M$ ) was usually equal 32 and  $N=16$  in BD simulation and  $N=16, 50, 100$  in SD simulation. The shear rate was due to movement of planes with constant velocity in opposite directions along the planes. We varied also both the grafting density and the distance between planes. In the case when shear is absent all the methods (BD, SD and MD) give the same density profile and other structure characteristics. But MD and SD methods are more effective than BD method because larger integration steps are available. We did not introduce the solvent explicitly so only BD and SD methods were suitable for shear simulation. It was obtained that chain elongation and inclination growth with shear rate. But elongation as function of inclination is more weak function than it follows from the theory of Rabin and Alexander or from more recent work of Barrat. The elongation of chain in the direction ( $x$ ) of shear is accompanied by decrease of chain size in perpendicular to shear direction ( $y$ ) along the plane. It was shown both by BD and SD methods that the height of brushes in the direction perpendicular to planes ( $z$ ) usually decrease (but lesser than  $y$ ) with increase of shear rate. But there is some region of parameters ( $N$ , grafting density, distance between planes) where at small shear rates the height of brushes increase a little. But to be sure that this is a real effect it is necessary to get results of more long calculations which are performed now. Effect of shear on dynamical properties was studied also. It was obtained that characteristic times of different correlation functions decrease with shear. It was shown that such decrease of characteristic times is mainly due to restriction of magnitudes of fluctuations with shear. This work was supported by Deutsche Forschung Gesellschaft and by Russian Foundation of Fundamental Research (grant N 96-03-33833a).



## SHORT AND LONG CHAINS IN A POLYMERIC BRUSH: A CONFORMATIONAL TRANSITION

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We consider conformations of admixed end-anchored macromolecules included into a homogeneous monodisperse planar brush and differing from the majority brush-forming chains only by their molecular mass. We concentrate on the case when the fraction of admixed macromolecules is small, and the average distance between them is large enough so that they do not feel one another and interact only with the majority chains.

We find that a minority chain can take three different types of conformation depending on its molecular mass (or polymerisation index,  $K$ ) relative to that of the majority chains,  $N$ . If the minority chain is shorter ( $K < N$ ) it forms a slightly deformed random coil, the average end height and its fluctuation being both proportional to  $K^{1/2}$ . A longer minority chain ( $K > N$ ) acquires an inhomogeneous flower-like conformation: its first  $N$  segments form a stem of height  $H$  equal to the thickness of the brush, while the rest  $K-N$  segments make a randomly coiled crown pushed outside the brush. The stem is strongly stretched (the average height of its end segment is  $\langle z_N \rangle = H \sim N$ ) but its fluctuations are small:  $\delta z_N \sim N^{1/3}$ . The transition from one type of the conformation to another occurs as the number of units in the minority chain,  $K$ , changes within a narrow range around  $N$ . In this regime, the chain takes an intermediate conformation that is simultaneously strongly stretched and strongly fluctuating:  $\langle z_N \rangle \sim \delta z_N \sim N$ .

When  $K \rightarrow N$  from the lower values, the coil deformation increases, and the end height fluctuation goes as  $\lambda^{-1/2}$ , where  $\lambda = N/K - 1$ , until it saturates at the value characteristic of the majority chains. When  $K \rightarrow N$  from above, the crown starts to penetrate the brush which leads to stem fluctuation increase proportional to  $\lambda^{-1}$ .

The transition from a coil to a flower conformation is discussed within the framework of the phase transition theory, and it is shown that the features of both the first and the second order transitions are present.

## POLYMER BEHAVIOUR IN A SHEAR FLOW NEAR REPULSIVE SURFACE.

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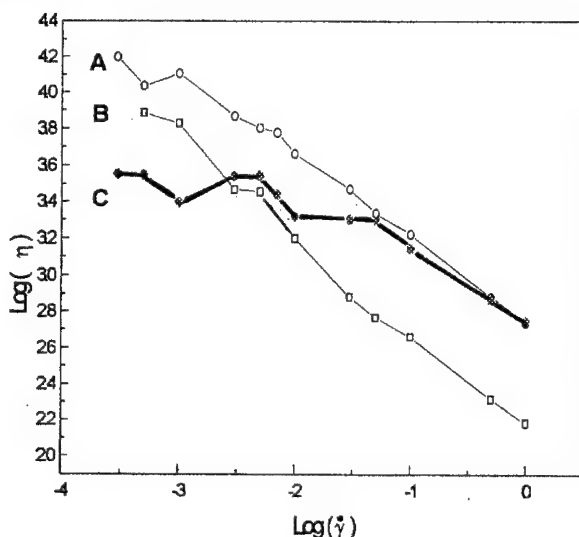
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The results of molecular dynamics computer simulations of a single polymer chain in simple shear flow are presented for two cases corresponding to the chain attached to a repulsive surface and the chain arranged far from the surface. We have used a bead-rod chain model consisting of 101 beads which are allowed to interact via Lennard-Jonse potential. Interaction of the chain with solvent flow was performed by collisional dynamics technique.

The effect of solvent flow is demonstrated through the dependencies of the various quantities describing the chain conformation (end-to-end distance, alignment angle, beads density distribution) and the rheological data (shear viscosity, normal pressure differences, surface attachment force) on the flow shear rate.

It is shown, that a shear flow field is more effective in stretching and alignment of the chain in the vicinity of the surface than far from it. At high shear rate the adsorbed chain is stretched twice as much as the free chain.

The influence of the solvent conditions (good, poor) and solvent viscosity on polymer behavior is also discussed (see Figure).



**Figure.** Shear viscosity  $\eta$  vs shear rate  $\dot{\gamma}$  curves for adsorbed (A,C) and free (B) chains in the good (A,B) and poor (C) solvent conditions.

## MOLECULAR DYNAMICS SIMULATIONS OF LIPIDS WITH POLYENE HYDROCARBON CHAINS

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The basis of biomembranes is provided by a bilayer consisting of phospholipids. There is increasing evidence that polyunsaturated lipid hydrocarbon chains play a fundamental role in ensuring the normal membrane functional processes. The knowledge of polyenoic lipids structure and dynamics is essential for our understanding of their functions on an atomic level. The experimental data on polyenoic phospholipid properties are very scarce. In this work, the behaviour of isolated lipid molecules has been analysed.

Molecular dynamics simulations of the lipids with unbranched polyene chains have been carried out. A polar head group was treated as an effective sphere with a Van der Waals interaction with the chain atoms. An sn-1-stearoyl (18:0) diacylglycerols that contained fatty acyl chains with 18 - 22 carbon atoms and various numbers of double bonds cis in the sn-2 position - oleoyl (18:1(n-9)cis), linoleoyl (18:2(n-6)cis), linolenoyl (18:3(n-3)cis), arachidonoyl (20:4(n-6)cis) and docosahexaenoyl (22:6(n-3)cis) - have been studied at various temperatures.

The potential energy function set used included the energy of nonbonded interactions, deformation of bond lengths (bond-stretching), valence angles (angle-bending), torsion angles, out-of-plane fluctuations of the double bonds and the carbonyl groups. All the hydrogens were treated explicitly. The alternative model with constant bond lengths has also been considered. Molecular dynamics modelling with and without ambient effects has been carried out; in the latter case the collisional dynamics method (A.S. Lemak and N.K. Balabaev) has been used.

According to the computer experiment results at low temperatures there is a strong tendency to cooperation between the two hydrocarbon tails. Polyunsaturated chain segment conformations turned out to be closely the extended angle iron - shaped one, but helical conformations of these segments have also been observed. At temperatures about 300 K the mean number of conformational transitions per torsional angle in polyenoic acyls is higher than those for stearoyl. Some structural and dynamical properties of the molecules have been discussed.

## DIFFUSION AND CONVECTION IN POROUS SOLIDS UNDER CHROMATOGRAPHIC BOUNDARY CONDITIONS

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In chromatography, porous materials in granular form are packed into columns. In this manner a second wide-diameter porous space is established between the beads in addition to the pores within the porous material. Solutes penetrate both porous spaces. Whereas the flow through the interstitial space is dominantly a convective process, it is widely believed that intra-bead transport can be explained by diffusion alone. However, a number of papers demonstrate that intra-bead convection amounts to a measureable contribution to peak dispersion even with standard HPLC-columns and operating conditions. Intra-bead convection increases resolution and thus is essential for improved performance. Interestingly not all experimental studies agree with the nowadays accepted calculation of convection by Rodrigues.

We may define a convective factor  $Cf$  which is a measure of intra-bead convection. In the laminar regime of geometric scaling (low Reynolds numbers) it is proportional to the ratio of bead diameter  $d$  and pore size  $R_{\text{pore}}$  as follows

$$Cf \propto \left( \frac{d}{R_{\text{pore}}} \right)^2$$

where the square originates from the Hagen-Poiseuille law. Experiments at low Reynolds numbers agree well with the theory of Rodrigues based on  $Cf$ . Experimental studies at intermediate Reynolds numbers ( $Re \sim 0.02 - 3$ ) can be brought to mutual agreement if it is assumed that the relevant convective factor now is

$$Cf^* \propto \left( \frac{d}{R_{\text{pore}}} \right)^1$$

The value of  $Re \sim 0.02$  for the transition is surprisingly low. In support of this, one study demonstrated that interstitial flow becomes convective rather than laminar.

# HYPOTHETICAL MODEL FOR THE PACKING OF CELLULOSE ACETOMYRISTINATE MACROMOLECULES IN LANGMUIR- BLODGETT (LB) FILMS

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The structure of cellulose acetomyristinate (CAM) with different compositions has been investigated by X-ray diffraction on passing from CAM in bulk via a solution to LB films. The position and half-width of SAXS reflections of CAM in bulk and in LB films at  $p=17$  mN/m, which characterize the interchain distance in macromolecules, are similar. Two SAXS reflections of LB films at 35 mN/m correspond to the bilayer thicknesses of 50 and 40 Å.

Taking into account these data and the great number of possible conformational transitions of cellulose and its esters, it may be assumed that CAM molecules packing in bulk and in LB films is determined by not less than two conformations at  $p=17$  mN/m.

In the process of further forced organization on a two-dimensional system on the subphase (up to  $p=35$  mN/m), a structure with two types of domains ordering is probably formed in LB films. Therefore, it is possible to represent a hypothetical model for packing of CAM molecules in LB films of the Y type. This model assumes the existence of a two-domain structure in which densely packed residues of the myristic acid are located on one side of glucoside rings and are oriented normally or at an angle to the backbone of the cellulose chain.

## NEW ASPECTS OF MOLECULAR ORDER FORMATION IN LANGMUIR- BLODGETT FILMS OF RIGID ROD-LIKE POLYIMIDE PRECURSORS.

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Ultrathin multilayer films of polyamic acids (PA) based on dianhydride of biphenyltetracarboxylic acid and two diamines p- phenylenediamine and o-tolidine (BP-Ph and BP- TD) were investigated.

Multilayer films (30 and 60 layers) of amphiphilic PI precursors (PC) were prepared from the solutions of polyamic acid (PA) and tertiary amines in mixture solvent DMAA:benzol and were deposited onto a Si substrate.

The structure of PC films was studied by SAXS, electron diffraction method and analysis of  $\pi$ -A isotherms

It is shown that the organization of the macromolecules of PC are profoundly affected by the chemical structure of the rigid chain of these polymers.

The stable LB films of PC on base of para- phenylenediamine (BP-Ph) were obtained directly by LB technique. Multilayers were Y-type films, and the thickness of the prepolymer bilayer was about  $53 \text{ \AA}$ . The area S per repetition unit in the monolayer on the subphase was  $120 \text{ \AA}^2$  ( $p=35 \text{ mN/m}$ ). It is possible to obtain the stable homogeneous films of PC based on o-tolidine (BP-TD) only by Shefer method. Films were z-type with the thickness of monolayer  $6 \text{ \AA}$  and  $S=135 \text{ \AA}^2$  ( $p=30 \text{ mN/m}$ ).

# LANGMUIR-BLODGETT FILMS OF FLUORINATED COPOLYMERS CONTAINING CHROMOPHORE GROUPS

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*V.Safronov\*\** and *L.A.Feigin\*\*\**

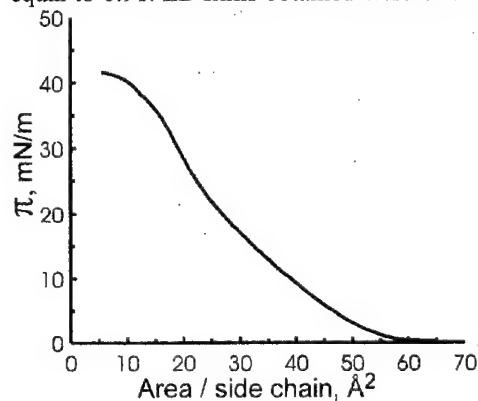
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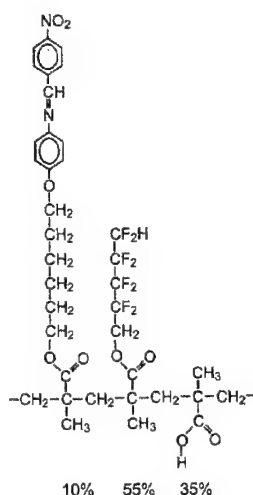
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Three-component random copolymers containing different portions of 6-[4-(4'-nitrobenzylidenamino) phenoxy]hexyl methacrylate, octafluoroamylmethacrylate and methacrylic acid comonomers were obtained by radical polymerization. One of them (see figure) was used for Langmuir-Blodgett (LB) film fabrication.

Such composition is based on our previous experience with more simple two-component copolymers [1]. Now we added comonomers with chromophore groups which are supposed to show non-linear optical properties. The copolymers obtained were characterized by IR, UV and NMR spectroscopy and measurement of characteristic viscosity in cyclohexanone. The contents of chromophore groups (as shown by NMR study) in the copolymer corresponds to that in solution of comonomers. The figure below presents  $\pi$ -A isotherm for the Langmuir monolayer of this copolymer at a water surface. The monolayer was transferred onto a hydrophobized silicon substrate at  $\pi=25$  mN/m. Transfer ratio was equal to 0.91. LB films obtained were of uniform interference color



that means uniform deposition over the substrate area. However, X-ray diffraction study did not reveal neither periodicity (no Bragg maxima were observed) nor overall film thickness uniformity (no Kiessig fringes). So, periodical structure of the film was not perfect and film surface roughness was significantly higher than the wavelength used (1.54 Å). The most probable explanation is that the difference of side chain lengths of comonomers prevents perfect multilayer formation. To obtain more ordered structure, we plan (1) to prepare alternating layer LB films and (2) to choose new comonomers with equal side chain lengths.



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## Polymer molecules orientation in top layers of polyamideimide films.

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The orientation of macromolecules in the top layer of dense porous aromatic polyamide-imide films (asymmetric membranes) has been investigated by angle-resolved XPS. Membrane characteristics in the separation process depend not only the chemical nature of the polymer used but also on the morphological features of membranes.

In the order to form asymmetric porous structures consisting of a dense skin-layer on the surface of a loose matrix (sublayer) from the same polymer, phase inversion process is generally used. During this process with polymer solution deviation into phases a gel (membrane basis) is formed. The asymmetric porous structure appears because of different conditions of gel formation in different cast film layers during diffusion in opposite directions of the components of the casting solution and precipitant. The gel structure is determined by polymer solubility in the system: polymer/solvent/nonsolvent (precipitant and/ or poreformer) and by the interaction between the components of the system. In this connection the composition of the casting solution plays an important role in structure formation of the porous film.

Phase separation mechanism (nuclear or spinodal mechanism) determines the gel structure and depends not only on polymer content in the casting solution but also on the nature of supermolecular fluctuations. The structure of these fluctuations in relationship to the chemical nature of the polymer used has not yet been elucidated. It may be assumed that mutual arrangement of the polymer molecules and the fragments in the gel, which appears during diffusion of the solvent and nonsolvent in opposite directions influences not only the pore characteristics of the membrane but also the fine structure of its surface layers.

The present paper is an attempt to establish these differences in a dense film and in anisotropic porous films of polyamide-imides. Porous films have been obtained in the solvent (N-methylpyrrolidone and /or dimethylacetamide)/nonsolvent (ethylacetate and/or ethyleneglycol) systems with different compositions by precipitation into an aqueous precipitation bath.

Films obtained under given casting conditions consist of a denser skin-layer with a pore diameter less than 120Å and a loose sublayer with finger-formed large pores in the cross section of this layer located normally to film surface.

The analysis of concentrations of carbon, oxygen, and nitrogen atoms shows that the mutual arrangement of the amine and anhydride fragments of polyamide-imide molecule on the skin-layer surface depends on the composition of the casting solution. The addition to this solution of a certain amount of the nonsolvent (ethyleneglycol) determines the predominant orientation of the anhydride fragments with respect to porous film-surface, which is different from that of these fragments in a compact dense film.



## ORDERING OF CASCADE POLYMERS IN THIN FILMS

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Due to an extraordinarily high degree of branching, dendrimers, cascade comb polymers and polymacromers, represent a particular type of macromolecules whose structure is developed in three dimensions. Topologically defined surface and colloidal size of the molecules justify to characterize them as *molecular particles* in which, however, molecular flexibility and surface overlapping should be taken into account. Interfacial organization of two kinds of molecular particles, e.g. carbosiloxane dendrimers<sup>1)</sup> and cascade comb polystyrenes<sup>2)</sup> on a solid substrate were investigated by Scanning Force Microscopy (SFM).

Tapping SFM allowed to visualize the aggregation process of carbosiloxane dendrimers starting from (i) single molecules which coagulated upon increasing the concentration to (ii) adsorbed clusters and (iii) fluid droplets followed by formation of (iv) a complete layer on the solid substrate. Single molecules were displayed as spherical particles with a diameter of about 2.5 nm. SFM of the liquid was possible due to the fact that the dendrimer undergoes a viscoelastic transition below the tapping frequency of about 360 kHz. Dynamic shear compliance  $J(\omega) = J'(\omega) - iJ''(\omega)$  experiments have shown that this viscoelastic state is characterized by a plateau compliance of  $5 \cdot 10^{-7} \text{ Pa}^{-1}$ . The droplets spread very slowly and yielded polygonal lamellar domains demonstrating that the constituting molecules underwent ordering.

Cascade comb polystyrenes, which are neither charged nor polar, showed a peculiar self-organization into a monomolecular film upon casting from solution on a solid, flat substrate. After evaporation of the solvent, the molecular spheres were not coalesced, remained distinct and hexagonally ordered. Depending on the branching density, shrinkage of the spheres perpendicular to the substrate was observed. Molecules with a high branching density ( $M_b \sim 500 \text{ g/mol}$ ) showed only little deformation and their spherical geometry recovered after annealing above the glass transition temperature of polystyrene. The observed phenomena were discussed in terms of the size, shape, rigidity and surface structure of the molecular particles.

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# THE ENERGY OF FINITE DISTORTION FOR MONOATOMIC FCC LATTICE

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The potential energy barrier and geometry of volume-conserving finite distortion for monoatomic fcc lattices in the absence of thermal motion are investigated. It is shown that orthorhombic transformation path can continuously transform a fcc crystal structure into one of six neighboring fcc crystal structures. Each of these new fcc lattices is equal to the original one and differs from it only by a rigid rotation. Any of its atoms changes only two atoms (from the total of 12 atoms in its first coordination sphere) into another pair of atoms. The height of the minimal potential energy barrier between the two neighboring stable fcc structures are calculated with Morse and Mie families of two-body potentials under constant volume extension or contraction. The barrier height is several times less than the energy, corresponding to dilatations where the lattice cohesion in practice is lost (melting energy). The total energy difference between body-centered and face-centered cubic crystal structures is equal to the minimal barrier height for large values of the effective radius of interatomic interaction. For small values of the radius the minimal barrier height is less than this difference. A growth of the effective radius of the interatomic interaction decreases the barrier energy height. The height strongly increases with volume contraction and decreases with volume extension of the fcc structures. Two kinds of tetragonal crystal structures appear at the volume extension which are locally stable with respect to the orthorhombic distortion of the monoatomic crystals with Morse and Mie two-body potentials.

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INFLUENCE OF CARBOXYL MODIFICATION OF DIPHILIC OLIGOMERS  
ON THE STRUCTURE OF THEIR ADSORPTION LAYERS ON LATEX  
PARTICLES.

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Adsorption of insulin, its receptor-binding fragment Arg-Gly-Phe-Phe-Tyr-Thr (I), and insulin-binding peptide Cys-Val-Glu-Glu-Ala-Ser (II), as well as diphilic oligomers Triton X-305 and X-100, their carboxyl derivatives, and their conjugates with II on carboxylated latex particles has been studied. It was shown that the method of adsorption binding of peptides was effective for I, which has hydrophobic structure and contains amino groups interacting with the carboxylated surface. At the same time the complementary interaction of I with II at the latex surface was not detected, perhaps, as a result of sorbate immobilization. However, the use of conjugates of diphilic oligomers with II not only permitted the adsorption binding of II with particles but also increased the accessibility of II during complementary interaction because of the presence of polyoxyethylene chain. It was found, that eventual plateau values increased in the following sequence: Triton X-305, its carboxyl derivative, and its conjugate with II, whereas in the case of Triton X-100 this sequence was reversed. It was supposed that multipoint interaction of diphilic oligomers with the surface changed to one-point binding by their hydrophobic end in the case of carboxylated derivatives and carboxyl-containing peptides. Electrostatic repulsion of end-carboxylated polyoxyethylene chains from carboxylated surface resulted in a decrease of the strength of its binding and of surface area per molecule of Triton X-305 derivatives. The replacement of Triton X-305 conjugated with II on the surface by Triton X-305 or Tween 20 confirmed these changes in the structure of adsorption layers.

## POLYMERIZATION OF THE ACRYLIC AND METHACRYLIC SURFACE-ACTIVE MONOMERS IN MONOLAYERS

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Polymerization of the surface-active monomers (SAM) in monolayers at the liquid/gas interfaces is the unique method for preparation of the highly ordered stable ultrathin films with desirable properties. But the kinetic of the SAM polymerization in monolayers, that is very important for understanding of the mechanism of this process, is not quantitatively described. This work is the comparative study of the kinetic of polymerization of acrylic and methacrylic surface-active monomers in monolayers at the liquid/gas interfaces.

The following surface-active monomers: N-acryloyldipalmitoylphosphatidylethanolamine (ACDPPE), N-acryloyloctadecylamine (ACODA), 12-oxo-10-octadecenoyl acid (ODA) and 1,2-di-(12-oxo-10-octadecenoyl)-glycero-3-phosphorilcholine (ODPC) were synthesized. It was found that the surface pressure - molecular area and surface potential - molecular area isotherms for monolayers of these surface-active monomers are completely different, depending on the position of the acrylic or methacrylic groups in the hydrophilic part, in the middle or at the end of the hydrophobic part of the molecule.

Polymerization of the SAM in monolayers was initiated by UV-irradiation ( $\lambda$  254 nm, 10 mW/cm<sup>2</sup>) in inert atmosphere. The rates of polymerization for SAM, having acrylic groups in the hydrophilic part of the molecule, for example ACDPPE, rapidly decrease with small increase of the surface pressure (from 2 to 5 mN/m), increase in the range of 5-14 mN/m and slowly decreases at higher pressures. The dependence of polymerization rate for SAM, having polymerizable groups in the hydrophobic part of the molecule, for example ODPC, vs. surface pressure has an opposite character. The rate of polymerization increases during the long range of surface pressures (between 5 and 35 mN/m) that correlates with increase of the degree of orientation of the fatty acid chains in this lipid molecule. After sharp maximum at 35 mN/m the rate of polymerization decreases with further increase of the surface pressure (until collapse of the monolayer), because of the monolayer "overcompression".

Thus, the differences in kinetics of polymerization of various acrylic and methacrylic surface-active monomers in monolayers can be explained by position of the polymerizable groups in the hydrophobic or hydrophilic part of the molecules. These monolayers were used for immobilization of various biologically-active molecules that makes them the unique systems for modeling of biomembranes and promising materials for advanced nanotechnology.

## POLYMERIC MONOLAYERS BASED ON LIPID-LIKE MONOMER WITH IONOSELECTIVE PEPTIDE - VALINOMYCIN

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The mixed monolayers of lipids and biologically active peptide-ionophores (such as valinomycin) are particularly useful, to our opinion, for the modeling of biological membranes. In our previous publications [1-3] monolayers of the valinomycin and its mixtures with phospholipids, having different structures and charges, were investigated at various aqueous salt subphases.

The main aims of this work are an investigation of the interactions between valinomycin, immobilized in the monolayers of the specially synthesized lipid-like monomer, with alkali metal cations from the aqueous subphase and polymerization of these mixed monolayers in order to stabilize the special conformations of the peptide.

It has been found that the surface pressure - molecular area and surface potential - molecular area isotherms for mixed monolayers of valinomycin and 1,2-di(octadeca-9,11-dienoyl)phosphatidylcholine (DODPC) are completely different depending on the kind of cation presented in aqueous salt subphases. Two additional states of valinomycin-DODPC monolayers are observed in the presence of  $K^+$  as compared to  $Na^+$  in the aqueous subphase. This phenomenon correlates with the strong complexation between the valinomycin and  $K^+$  in bulk. An influence of zwitterionic head group of the lipid-like monomer DODPC on the binding ability of valinomycin to cations at the interface has been investigated. The polymerization of monolayers of the pure lipid-like monomer DODPC and its mixtures with valinomycin has been initiated by soft UV-irradiation (254 nm). The rate of DODPC polymerization in monolayers is relatively high and strongly depends on the applied surface pressure (maximum is  $2.25 \cdot 10^{-4} \text{ s}^{-1}$  at 20 mN/m), but rapidly decreases with the increasing peptide molar fraction in the mixed monolayers. The possibility of the stabilization of valinomycin conformations by polymerization of these mixed monolayers has been shown.

Thus, the valinomycin-DODPC monolayers are the unique systems for the modeling of the molecular recognition phenomenon in the biological membranes and can be used as highly sensitive materials for the ion-selective electrodes.

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## SYNTHESIS AND POLYMERIZATION OF THE 12-METHACRYLOYLOXYDODECANOIC ACID AND LIPID IN MONOLAYERS.

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The following surface-active monomers with metacrylic group at the end of hydrocarbonic chains: 12-methacryloyloxydodecanoic acid (12-MAODA) and 12-(methacryloyloxydodecanoil)-glycerophosphatidylcholine (12-MAODG) were synthesized and investigated.

There are two regions with different slopes on the surface pressure ( $\pi$ ) - area per molecule (A) isotherm for 12-MAODA, which can be assigned to the two states of monolayer: liquid-expanded (at  $\pi$  below 12 mN/m) and liquid-condensed (in the range of  $\pi=13-28$  mN/m), respectively. In contrast, only one state (liquid-expanded) has been observed for 12-MAODG. This difference can be explained by influence of dimension of the hydrophilic "head" on the surface-active properties of this monomers.

These monomers have been polymerized in the monolayer at the liquid/gas interface by soft UV-irradiation (254 nm). Dependences of polymerization rate vs. surface pressure have maximum in the range of  $\pi=7-10$  mN/m for both monomers. Maximal polymerization rate of 12-MAODG ( $3.33 \cdot 10^{-4} \text{ s}^{-1}$ ) is less than that one of 12-MAODA ( $4.89 \cdot 10^{-4} \text{ s}^{-1}$ ). The higher rate of 12-AODA polymerization as compared to 12-MAODG is due to the more dense packing of acid molecules in monolayer as compared to the lipid. 12-MAODG has much larger area of the hydrophilic "head" in comparison with the only one "tail" that disturbs the regular packing of these monomer at the interface.

Areas per monomer unit in the obtained polymeric monolayers are much smaller than those for the monomer one that correlates with the monomer contraction in the volume during polymerization. The absolute values of these areas decrease with increasing surface pressure at which the polymerization takes place. The collapse pressures increase after monomer polymerization that evidences the increase of the monolayer stability in case of polymer as compared to monomer.

These polymeric monolayers can be used for the immobilization of various biologically active substances.

## ASSOCIATIVE-DISSOCIATIVE PROCESSES OF SUBUNITAL PROTEIN'S MOLECULES AS A MAIN REASON OF CHANGE OF THEIR THERMOSTABILITY

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Studying of the nature of subunital macromolecules and their components interaction is a central problem for molecular biology and biophysics. Result of this interaction is, frequently, association or dissociation of the macromolecules depending on nature of influencing physical and chemical agents. Modification of proteins by the latters allows us to discover their functioning mechanisms in different microenvironment condition as well as to link the detected functional damages with interaction types (association-dissociation) of studying proteins. Because the establishment of nature of the powers and interactions which are stipulates the associative and dissociative processes into protein's molecules is necessary.

It has been shown on base of determination of the P50 and Hill's constant values that temperature increase of aqueous solutions of the mice hemoglobin to 42-45 °C induced the accumulation of "super-tetramer" forms of hemeprotein owing to formation of additional (probably weak) bonds.

It has been determined that oxyhemoglobin molecule at present of 0.05-1 mol/l NaCl shows as tetramer and dimer mixture, in tris-glycin buffer (pH 8.3) - trimers and monomers, in 0.1 mol/l phosphate buffer (pH 6.4) - dimers and monomers.

The process of temperature denaturation of the superoxid dismutase proceeds by two stages with activation energy values 14.8 and 155.5 kJ/mol in temperature intervals 20-70 and 70-85°C. At the 20-60°C there are reversible conformation changes in superoxid dismutase molecules because of sequence unfolding and folding of protein's globule. In case of lactate dehydrogenase's thermoinactivation determined four stages with activation energy values 24.4; 151.1; 91.9; 33.0 kJ/mol accordingly for temperature intervals 40-45, 45-50, 50-60, 60-70°C. The reason of LDH thermoinactivation in these temperature diapasons is dissociation of enzyme's molecule to monomers and following re-association of subunits. Thus taking into account of high ability of oligomer macromolecules to dissociation-association together with change of functional activity level is necessary at the investigation of physical and chemical principles of functioning of the oligomer proteins in different microenvironment.

## IMMOBILIZATION OF AMILOLYTIC ENZYMES ON THE ION-EXCHANGING ROSINS

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Application of immobilized enzymes in different fields of industry promote their multiple using as biocatalisators, reduction of prices of the final product's separation, creation of the wasteless industrial technology.

The physically-chemical characteristics of immobilized enzymes such as glucoamilase (alfa-1,4; 1,6-glucoanhydrolase) which decompose alfa-1,4 and alfa-1,6 bonds of starch and inulase (alfa-2,1-D-fructanfructanhydrolase) which chipping off the fructose's residues from non-reducing part of inulin molecule (reserve polysaccharide of plants) have been studied in the paper.

We are tested near 20 ion-exchangers, prepared to immobilization by conditioning: carboxylic cationites of different sewing and porosity degrees, low-basic anionites of polycondensive type, polyacrilonitrilic fibers. We are conducted immobilization by the adsorbtion and covalent methods (azide, glutarate aldehyd, anhydride, chloranhydride etc.). Catalitical activity of glucoamilase was determined by the glucose oxydase methodbut inulase by means of resorcyne, containing of protein in immobilized enzymes by the modified Loury's method, the character of bonds verified by the IR-spectroscopy method. It has been shown that enzymes keeps 20-70% of catalitical activity relative to free enzymes. The type of carrier and character of bond are very important of hydrolitic ability for protein.

It has been ascertained that glucoamilase immobilized on the KB-2 0.5 by the modified amin method (lengthening of linking chain between enzyme and carrier) has a better catalitical properties.

Binding of amilases with ionites leads to increase of stability of the enzyme relative to native enzyme - the interval of optimal pH value increases on the unit, temperature optimum shifts to the higher temperatures on the 10°C (at the adsorbtion method of immobilization) and on the 20°C at the chemical. Ion-exchanging materials may be used as a carriers for the glucoamilase and inulase immobilization. In this case the taking into account of their structure is necessary. The priority have ionites with chemical affinity to immobilized enzymes.



**THE INFLUENCE OF UNSATURATED CARBOXYLIC ACID  
RADICAL LENGTH ON THE INTERACTION OF N-VINYL-  
PYRROLIDONE POLYANIONS WITH CATIONIC SURFACE  
ACTIVE COMPOUND.**

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Copolymers of N-vinylpyrrolidone and unsaturated acids are known to be non-toxic and blood compatible and suitable for modification of biologically active compounds. Macromolecular conformation in water solutions is of great importance for utilization of polymer for biologically active compounds modification.

The copolymers of N-vinylpyrrolidone (VP) with unsaturated acids - acrylic (VP-AA), vinylacetic (VP-VA), undecylenic (VP-UA) - were synthesized, the content of carboxylic groups been from 5 up to 20 mol.%, and average molecular weight was about 100000.

The viscometric measurements showed that the size of VP-UA macromolecular coil is lower than that of VP-AA macromolecular of the same degree of polymerization on account of interactions of hydrophobic radicals of the VP-UA copolymer.

The interaction of synthesized polyanions with cationic surface active compound-dimethylbenzylaurilammonium bromide (DMBLAB) was studied by light-scattering and viscometric methods.

The interaction of VP-AA and VP-VAA copolymers with DMBLAB is accompanied by macromolecular association, that is not observed in the case of the DMBLAB interaction with VP-UA copolymer of the same composition as VP-AA and VP-VAA and concentration in solution (0,01 g/ml).

**Order and Motion of Poly(oxyethylene)-poly(oxypropylene)  
Triblock Copolymers in Aqueous Solutions and in Adsorption  
Complexes with Polystyrene Surfaces as Assessed by the EPR  
Spectroscopy.**

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The micellization of poly(oxyethylene)-poly(oxypropylene) triblock copolymers (PEO/PPO/PEO, Pluronics) in aqueous solutions was investigated using the EPR technique. A paramagnetic amphiphile, 16-doxyl stearic acid was used to assess the order and motion of the hydrophobic PPO blocks depending on their size and PPO/PEO ratio. When comprised of long PPO and short PEO blocks, Pluronic manifested three regions on phase diagrams: unimers, loose aggregates penetrated by water, and dense micelles with hydrophobic cores. No dense micelles were formed in case of long PEO blocks (at the same length of a PPO block).

To investigate a motion of PEO blocks, the terminal hydroxyl group was modified by a spin label, 3-carboxyproxyl. The motion of the PEO chain end was decreased upon the formation of dense micelles.

PPO block was found to be completely immobilized upon adsorption on PS surface, whereas the motion of PEO chain depended on its length and the degree of surface coverage.

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## **STRUCTURE AND CORRELATIONS OF CHARGED DIBLOCK COPOLYMERS IN AQUEOUS SOLUTIONS**

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We present various experimental evidences of the existence of micelles in charged block copolymer aqueous solutions. A special care has been taken to discriminate the behaviours with respect to those encountered with polyelectrolytes. In particular the effect of counterion condensation will be discussed both from the theoretical and experimental points of view. The above results lead to consider these micelles as charged brushes of spherical symmetry. Correlations between micelles have been also studied by neutron and X-ray scattering and a liquid-like order between micelles is found.

# THE OPTICAL CONSTANTS AND POLARIZABILITY SPECTRA OF FINITE REGULAR CHAINS AND LINEAR MACROMOLECULES AT THE INTERFACE SOLUTION- MONOCRYSTAL BY INFRARED SPECTROSCOPY

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Infrared ATR spectra of epoxydian oligomers (EO), polystyren (PS), and polyethylene (PE) in bulk of the solution and at the interface liquid (solid)-solid (KRS-5 and germanium (Ge) monocrystals) in IR regions of polymer absorption have been investigated. Based on Frenel and Kramers-Kronig procedures, spectra of optical constants (dispersion of the index of refraction and unitless index of absorption) were calculated for individual bands of EO, PS, and PE under changes of the unitless parameter  $[\eta]c$ . Within Loren-Lorenz approximation, taking into account the effective field of a light wave, spectra of real and imaginary polarizability  $a(\nu)$  of the macromolecules were calculated, as well as the orientation parameter  $s$  at the interface solution-monocrystal. It was found that the orientation of oligomer molecules (the degree of polymerization,  $DP \approx 2$ ), the length of which is smaller than that of the Kuhn segment, is at its maximum on KRS-5 at  $[\eta]c \approx 1$ . Parameter  $s$  was found equal  $s \approx 0.3$  for  $DP \approx 5$  at  $[\eta]c \approx 4.5$ , molecules being oriented at angle  $45^\circ$  with the respect to normal to the surface, and the continuous network structure in bulk of solutions and concentration surface excesses of EO corresponding to  $[\eta]c > 2$ . It was found for PS ( $M_N = 5.14 \cdot 10^5$ ) and PE ( $M_W = 1.85 \cdot 10^5$ ) that the maximum of orientation ( $s$ ) and polarizability ( $a$ ) of macromolecules at the surface of crystals correspond to  $[\eta]c < 1$ , and the length of the parts of macrochain being in contact with the surface is equal to the Kuhn segment. The rise of  $a$  at  $[\eta]c \geq 5$  is caused by crystallization of PE in bulk of the solution.

# THE STRUCTURE OF MICELLAR SOLUTIONS OF GELATIN IN THE SYSTEM IZOCTAN-WATER-BIS(2-ETHYLHEXYL) SODIUM SULFOSUCCINATE (AOT) ON THE TRESHOLD OF GEL FORMATION

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Dependence of the relative viscosity of micellar solutions (MS) of gelatin in the system izooctan-water-AOT on concentration of gelatin  $c=0.1-6.0 \text{ g dl}^{-1}$  at the ratio of concentrations  $[\text{H}_2\text{O}]/[\text{AOT}]=40$  has been investigated. Within frames of scaling approach, under the condition  $p_c \approx 0.31$  ( $p_c$  - the critical index of three-dimensional space), critical concentrations  $c(p_c)$  and  $c(1-p_c)$  of gelatin, the probability  $p$  of cluster formation, the mean polymerization degree  $s$  of fractal clusters, the width  $\Delta n$  of the sol-gel transition were calculated under changes of a polymer molecular weight  $M_v$  ( $(5.2-11.0) \cdot 10^4$ ) and temperature of solutions (293-305 K). The probability  $p([\eta]c)$  of the formation of infinite (or percolation) cluster in MS as a function of the unitless parameter  $[\eta]c$  is in consistence with the curves of the critical phenomena within the region of the sol-gel transition. The phase transition sol-gel in MS is complete at  $p \geq 0.69$  and  $[\eta]c < 1$ , and the width of the phase transition  $\Delta n = [c(1-p_c) - c(p_c)]/M_v$  depends inversely on the hydrodynamic volume  $V_o$  of macromolecules,  $V_o = [\eta] M_v$ . The size of micelles changes within the range of 190-340 Å at  $c(1-p_c)$  under variation of  $M_v$  of gelatin and the temperature of MS. The scaling relationship  $s = (\Delta p)^{2.7}$  was found for the mean polymerization degree. The possibility to control the size of micelles allows synthesis of microcrystals AgHal and Ag with a narrow size distribution in MS of gelatin.

## **Structure and Rheological Behaviour of Concentrated Suspensions of Swollen Latex. Experiment and Modelling.**

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Above a certain concentration  $C^*$  latex particles swollen in a good solvent form a gel. The system possesses a yield stress and a recoverable deformation below the yield stress value. The birefringence measurements show that latex particles under the shear deformation are oriented at  $45^\circ$  to the shear direction.

The proposed model of the single particle is based on the existing models of polymer brushes and networks. The minimisation of the free energy of a single particle and a particle under the deformation makes it possible to calculate the  $C^*$  and the gel elastic modulus. The calculated values of  $C^*$  and of the elastic modulus are in reasonable agreement with the experimental data.

The variation of the parameters of the model and the Flory exponent  $\nu$  gives the dependence of the gel elastic properties on the latex particles structure and solvent quality.

## THE EFFECT OF STRUCTURES ON TRANSPARENCY IN POLYMERIC LIGHT GUIDES

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The transparent amorphous polymers are widely applied in fiber optics. Since there are high transmission losses of light in polymeric optical fibers (POF), the important problem is to improve their transparency. The role of light scattering (one kind of it is scattering on heterogeneities of the polymer structure) is especially great in visible range of spectra, in which light guide is applied.

The effect of polymer morphology on transparency has been studied in the present work.

The cylindrical samples from polymethylmetacrylate (PMMA) with diameter 15 mm and height 100 mm and POF on their base were investigated by visible, IR spectroscopy, light scattering technique and transmission electronic microscopy. Initial polymer was produced by radical polymerization in block. The morphology of polymer was changed by the conditions of the synthesis and following moulding.

As a results of research conducted was found:

1. The value of light scattering of solid PMMA essentially depends on conditions of the synthesis. Increasing the temperature of the synthesis  $T_s$  from 70 to 115 °C was resulted in marked decreasing light losses on scattering. The reduction of the degree of PMMA syndiotacticity was led to appearance of less ordered and intense structure, that accompanied with decreasing light losses on scattering. The average dimension of scattering ordered ranges reduced from 40 to 30 nm with raising  $T_s$ .
2. The following annealing PMMA at 130 °C for 5 h was led to equalizing light scattering and structural properties in both samples obtained at different  $T_s$ .
3. Changing the parameters of POF moulding (the temperature and the speed of extrusion) caused transformation of dimensions of scattering ranges and value of light scattering.

The data obtained are taken into consideration making POF with high light transmission.

## FORMATION OF SELF-ORGANIZED DISCRETE MULTILAYERS IN BLENDS OF MESOPHASE POLYORGANOSILOXANES.

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Some novel linear and cyclolinar polyorganosiloxanes (CLPOS) without classical mesogenes in their macromolecules can form thermotropic mesophases which can be classified as columnar mesophases. It has been established by us that similar to PDMS, which is known to be able to spread and form thermodynamically stable monolayers on air-water interface (Langmuir's method), most CLPOS studied are also capable of spreading and building monolayers. Unlike PDMS CLPOS form stable self-organized discrete multilayers the thickness of which depends on the surface pressure. The transition from the monolayer to bi-, tri-, (up to seven) layers is reversible in cycle "compression-expansion" and characterised by sharp steps in  $\pi/A$ -isotherms. For more than ten samples a linear dependence of the pressure jump value of steps versus isotropization temperature has been found. A model has been suggested in which the steps are treated as a result of sliding macromolecules organized in columnar mesophase from layer to layer without breaking hexagonal order.

The aim of our study was to extend the model to the formation of multilayers in various blends of polysiloxanes on air-water interface. In two component blends three thermodynamical case may be realised: completely immiscible, partly and fully miscible mixed surface films. In fully miscible mixed film hexagonal structure was broken (mesophase is out) and surface isotherm is followed the additive rule. Self-organization of multilayers is impossible in this case. Completely immiscible mixed films form multilayers independent of each other polymers, as mesophase order preserves in domains.  $\pi/a$  - isotherms for partly miscible blends depend on composition of blends. The blends of PDMS (of different molecular weight) and polydecamethylcyclohexalinear siloxane, polyhexamethyl- and polyhexapropyl- tetracyclolinar siloxanes were investigated. The model suggested was confirmed by these experimental data.

Work supported by INTAS Foundation (grant 93-753), SFB-239 (University of Ulm), RFFI.



## DETECTION OF AMPHIPHILIC POLYMERS MICRODOMAINS IN AQUEOUS SOLUTIONS BY USING VARIOUS FLUORESCENT POLARITY PROBES

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In the last few years, many physico-chemical studies have been undertaken on organized systems acting as hosts for hydrophobic molecules, in order to highlight the structure of these assemblies. Among the techniques encountered in the literature, fluorescence spectroscopy, usually with pyrene as a probe, was used for amphiphilic polymers in aqueous media to provide useful information through the modifications of the microscopic environment of the chromophore. Unfortunately, polymers with long alkyl chain quaternized pyridine rings as repeat units are efficient quenchers for pyrene. Our objective was to find fluorescent probes, still sensitive to polarity changes but with short enough excited state lifetime to reduce or suppress the quenching processes. These required features led us choose fluorescent molecular rotors (*e.g.* cinnamylidene type molecular rotors).

Here, we report on the results about the detection of association phenomenon in the case of new cationic amphiphilic polymers series by using as a probe :

- pyrene for copolymers whose hydrophobic part is composed of N-dodecylacrylamide units and hydrophilic part, by quaternized (by methyl bromide) pyridinic moities : poly(N-dodecylacrylamide-*co*-1-methyl-4-vinylpyridinium bromide)s,

- cinnamylidene rotor for long alkyl chain copolymers derived from 3-vinylpyridinium salts : poly(1-methyl-3-vinylpyridinium-*co*-1-hexadecyl-3-vinylpyridinium dibromide)s. In this case, the use of pyrene is excluded due to quenching processes.

- both pyrene and cinnamylidene rotor for homopolymers poly(3-hexadecyl-1-vinylimidazolium bromide), in order to make a comparison between the microenvironment polarity detected by the two types of fluorescent probes.

## A NEW AMPHIPHILIC CATIONIC POLYMER DERIVED FROM 3-VINYLPYRIDINE : SYNTHESIS AND BEHAVIOUR STUDY IN AQUEOUS MEDIUM

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Combining the structure of linear polymers and of low molecular weight micellar compounds, amphiphilic polymers have been of particular interest in a wide range of potential applications since the 1950ies. Only for some years the attention has been focused on the understanding of the behaviour of that class of polymers in aqueous solution which strongly depends on their chemical structure. As a matter of fact and because of their conformation in water, these polymers are known for their tendency to form hydrophobic microdomains. These latter are able to incorporate organic compounds slightly soluble in water but soluble in organic media.

The purpose of this work is to describe the synthesis and the behaviour study in aqueous medium of a new amphiphilic cationic polymer derived from 3-vinylpyridine (poly-N-hexadecyl-3-vinylpyridinium bromide). This polymer is obtained by bulk free radical homopolymerization of the corresponding pyridinium salt using AIBN or ADVN as initiators.

In order to study the influence of the polymer concentrations and the composition of the n-propanol/water dissolving medium on their aqueous solution properties, various physico-chemical techniques such as viscosimetry, solvatochromic effects and cryo-transmission electron microscopy have been used. The solution behaviour of the poly-N-hexadecyl-3-vinylpyridinium bromide is compared with that of its low molecular weight analogue (N-hexadecyl-3-ethylpyridinium bromide) which behaves like a new surfactant but with conventional micelles properties. The viscosimetric measurements, which have been carried out in various n-propanol/water mixtures, clearly indicate that the hydrophobic microdomains appear from a low water content. The same effect, in terms of polarity change of the polyamphiphile microenvironment, have been detected by solvatochromic effects study using some specific probes.

For characterizing adequately the structure of this polymer in aqueous solution we have used cryo-transmission electron microscopy which reveals that our homopolymer adopts a finger prints like-shape. This method allowed us to determine, using the Tanford's model, the characteristics of the hydrophobic microdomains such as, diameter, macromolecule length and aggregation number.

## STABILITY OF COLLOIDAL SYSTEMS: FINE COLLOIDAL PARTICLES - ULTRA LARGE POLYMER MOLECULES

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The effectiveness of flocculation process induced by polymer depends on the polymer molecular weight. The ability of polymer to flocculate suspensions increases initially, goes through the maximum, and finally decreases with increasing molecular weight. A polymer of very high molecular weight hardly causes the bridging flocculation of fine suspensions. The work presented deals with the problem: why the flocculation effectiveness of ultra large linear polymers deteriorates with the 'increase' in molecular weight?

It was observed experimentally that many particles can be attached to a single macromolecule when the size of polymer coil considerably exceeds the size of particles. If the polymer chain is long and the number of particles is small, the aggregate structure is 10 s the particles can move more effectively than the whole aggregate. The Brownian walk of particle built-in the aggregate is limited to the space specified by the length of the polymer chain. Assuming that the quasi-free Brownian walk of particle depends on the size of polymer, chain and on the number of particles attached to it, we have evaluated the diffusion coefficient of built-in particle,  $D_p$ .

At the equilibrium of the colloidal system two opposing tendencies: sedimentation and diffusion are equal to each other. The equilibrium can be described by hysometric law which describes a one parameter particle density profile against the vertical coordinate. The parameter, called the gravitational length,  $L$ , is determined by the properties of particles. We have shown that since  $L$  is a function of  $D_p$  it also depends on the aggregate structure.

The stability of colloidal system can be concluded from the sedimentation equilibrium. The analysis of influence of the aggregate structure on the system stability indicates that the decrease of number of built-in particles and increase in size of polymer coil (which depends on molecular weight of polymer and solvent properties) enhances the stability of the system. It means that the increase in polymer molecular weight causes the deterioration of its flocculating ability for systems satisfying the model assumptions.

Assuming that the number of particles attached to a single macromolecule is a random number we have calculated the distribution of aggregates of different size both for the reversible and irreversible binding of particle to polymer. The number and size of all types of aggregates present in the system have been determined at different initial particle/macromolecule number ratios. The calculations of sedimentation equilibria for all types of aggregates give the destabilization efficiency of colloidal system versus the relative polymer concentration. We have shown that for the model system the optimum flocculation concentration of the polymer exists and that the decrease in the size of macromolecular coil can enhance the effectiveness of ultra large linear polymer to flocculate the suspension of very fine particles.

The predictions of the model presented are compared with experimental results on the stability of system composed of very high molecular weight polyacrylamide and fine colloidal AgI particles.

ESR SPIN-LABEL EVIDENCE OF PROTEIN CLUSTERS  
(CRITICAL MICROEMULSION) FORMATION IN WATER-SALT  
SOLUTION OF SERUM ALBUMIN MOLECULES

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Proteins display more or less pronounced tendency to long-range interactions and aggregation. This relates proteins to colloids. Stability of colloids (and proteins) is known to differ essentially with changing salt concentration. Sometimes it leads to phase transitions. Phase properties of solutions are described by phase diagram but very few of them are developed for proteins.

Molecules of serum albumin were modified by maleimide spin-label in Cys-34 position. The crevice where Cys-34 is located fluctuates between "closed" and "open" states differing by the accessibility to solvent. Effective thermodynamic parameters of activation of label transition between these states in  $MgCl_2$ ,  $CaCl_2$ ,  $NaCl$  solutions within concentration range of 0.001 to 4 mole/l were determined. Protein concentration was varied from 50 to 200 mg/ml.

Phase transition from "low salt" to "high salt" structure of protein solution accompanied by the rise of disjoining pressure in water-protein matrix has been shown to occur in the range of 0.01 to 0.1 mole/l salt concentrations. This fact, together with the analysis of spectral line width and anisotropy of protein diffusion provide information about long-range ion-electrostatic, hydration and molecular interactions of protein clusters (i.e. dynamic heterogeneities in which the local protein concentration is noticeably higher than volume-average protein content) forming in this transition zone. Probably clusters represent stabilized kinetically nuclei (or remains) of more ordered "low salt" phase.

Two kinds of phase diagram has been proposed to clarify the structures of protein solution: isotherms of Van-der-Waals type and triangular diagram. The latter is similar to that of two salts with common ion and bears features of the diagram of water-oil-surfactant system. Hence transition zone of colloid solubility of protein caused by dynamic clusters analogous to critical microemulsion.

## STRUCTURE STUDY OF SOME COMB-SHAPED COPOLYMERS IN A BULK AND THIN FILMS \*

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The structure of liquid crystal copolymers and copolymeric Langmuir-Blodgett films based on chiral  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}(\text{CH}_3)-(\text{CH}_2)_2-\text{COO}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{O}-\text{C}_8\text{H}_{17}$  and achiral  $\text{CH}_2=\text{CH}-(\text{CH}_2)_6-\text{O}-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{O}-\text{C}_8\text{H}_{13}$  monomers was investigated with a help of X-ray scattering method. Ni-filtered  $\text{Cu K}_\alpha$  radiation was used. The copolymers had mole content of the chiral component equal to 0.25, 0.50 and 0.75.

The bulk copolymer samples were prepared by free radical polymerization and oriented by magnetic fields in cooling from isotropic phase. X-ray diffraction data obtained in wide temperature range were interpreted with a use of a paracrystal model. All investigated copolymers have two each of tilted smectic phases with bilayer structures but their X-ray patterns show some features of intensity distribution in reflections related to the ratio of the chiral and achiral components. Thus 0.25 and 0.75 copolymers oriented in magnetic field have X-ray patterns corresponding shevron and book-shelf structures accordingly.

The copolymeric LB films were fabricated by UV polymerization of monomeric multilayers and by deposition of monolayers of monomeric molecules formed on water surface after their UV polymerization directly in monolayer. The source monolayers had the same contents of the chiral and achiral components as the bulk samples. Produced copolymeric LB films have some structural differences dependent on the content of the components and conditions of their formations including conditions of polymerization.

The correlation between the structure of comb-shaped molecules, the onelayer or bilayer structure of LB films and bulk smectic phases and the chirality of latter is considered using a molecular simulation and diffraction calculations from structure models.

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# Processes of the metal coordination polyurethane self-assembly and their connection with physical- mechanical and electrical properties

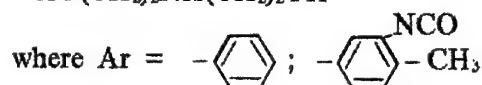
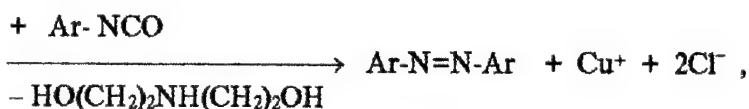
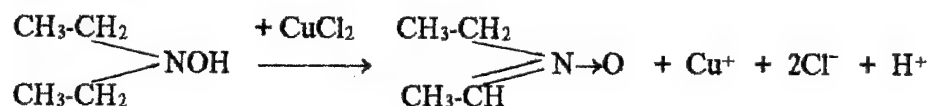
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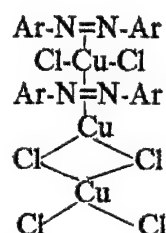
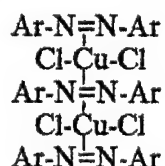
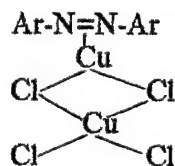
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Metal complexes have been synthesized on the basis of the cupric or ferric chlorate and N,N'-diethylhydroxylamine (DEHA) for chemical modification of polyurethane structure.

The scheme of interaction  $\text{CuCl}_2$  with DEHA and aromatic isocyanates is following:



The product of following complex formation of azoaromatic combination with  $\text{Cu(I)}$  and  $\text{Cl}^-$  - ions given below:



The nature of coordinated connection of 3d-metal ions with a polyurethane chain have been revealed. As a result of metal complexes addition to polyurethanes formation of the coordinated connection on ends hard blocks takes place that promotes their consolidation and extends microphase division in metal coordinated polyurethanes.

The research is supported by the Russian Foundation of Fundamental Investigations.

## PECULIARITIES OF THE SUPERMOLECULAR STRUCTURE OF POLYAMIDE-IMIDE ASYMMETRIC MEMBRANES

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Asymmetric microporous polyamide-imide membranes suitable as supports in composite membranes for separating gas mixtures have been synthesized. Permeability and selectivity of composite membranes depend on both the supermolecular structure of the surface skin layer and the surface porosity as well as the morphology of the sublayer of the support.

Scanning and transmission electron microscopy (SEM and TEM), atomic force and scanning tunneling microscopy (AFM and STM) have been used for the investigation of the morphology and the supermolecular structure of the surfaces and cross-sections of supports.

The membranes were prepared under identical conditions (the solvent, intrinsic viscosity of the polymer, concentration of the casting solution, post-treatment temperature and duration) from polyamide-imides differed in the chemical structure of the amine fragments (fluoro-containing or not) by wet formation in an aqueous precipitating bath.

Membrane structure can be satisfactorily explained in terms of the hydrophilic-hydrophobic properties of polymers used and mobility of polymer chains during the structure formation by liquid-liquid phase separation.

The size, structure, distribution and organization of pores in asymmetric polyamide-imide membranes are discussed in connection with their transport and separation properties.

## SUPERMOLECULAR ORDER IN POROUS SYSTEM OBTAINED BY EXTENSION OF ORIENTED HARD ELASTIC POLYETHYLENE SAMPLES

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Hard elastic polyethylene samples have been obtained by the crystallization at a high melt flow velocity and crystallization temperatures much lower than the melting temperature, and subsequent annealing. Porous systems are formed during uniaxial extension of hard elastic samples in the orientation direction.

It was observed that permeability of porous systems strongly depends on the degree of melt extension characterized by the spin draw ratio  $\lambda_s$ . At  $\lambda_s < 16$ , impermeable porous structures are formed; at  $\lambda_s = 16$ , the permeability appears and then increases with increasing  $\lambda_s$ . The appearance of permeability indicates that through flow channels are formed in the porous structure.

The supermolecular structure of impermeable and permeable samples as a function of  $\lambda_s$  has been investigated by the scanning electron microscopy technique. The difference in details of the supermolecular structure for two types of samples was discovered; and the sizes of the dense regions, the depth of pores, and also the distribution of pores over the sample surface were estimated.

A large amount of dense material without pores is observed on the surface of impermeable samples. There is a number of pores with a small depth in these samples, but through flow channels are absent.

For the permeable samples increase in the part of the surface occupied by pores has been observed, and the sizes of pores decreased. Pores have more symmetrical shapes, and their depths increases.

The electron microscopic investigations have shown that an increase in  $\lambda_s$  leads to a decrease in the fraction of the dense part of the structure. A decrease in pores' sizes and increase in their depths is seen on the electron microscopy pictures. The distribution of pores over the sample surface becomes more uniform and a number of tie extend elements of the supermolecular structure connecting the edges of pores decreases with  $\lambda_s$ .

The results of electron microscopic investigations of the porous structure confirm the data obtained by measurements of permeability for these structures as a function of the degree of melt extension. These observations are consistent with the model of the supermolecular structure of hard elastic samples presenting it as a system of large parallel lamellae lying perpendicular to the orientation direction. These lamellae are capable to move apart and to bend in the process of their uniaxial extension, and, as a result, to form pores between them.



## **Effect of the polymer structure and molecular parameters of sulfonated polyphenylene oxide on gas transport properties of membranes**

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Diffusive gas separation is based on different permeabilities of a polymer membrane for individual gases. The permeability is governed by the structural order in the membrane-forming polymer. The supermolecular structure of polymers is determined by a number of factors and one of them is the polymer-solvent interaction which originates in concentrated polymer solutions during membrane formation.

The goal of this work is to study the gas transport properties of polymer membranes as a function of polymer structure and molecular parameters resulting from polymer interactions with different solvents. The polymer investigated was sulfonated polyphenylene oxide (SPPO) which exhibits polyelectrolytic properties in the solutions of dimethylacetamide (DMA) and methanol that are used in this work.

Gas transport properties were examined by passing He, N<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub> through homogeneous membranes (30-40 μm thick SPPO films) or through composite membranes consisting of an SPPO selective top layer (1-5 μm thick) on a PPO microporous support.

It was shown that the inclusion of sulfonate groups in the polyphenylene oxide (PPO) chain profoundly affects gas transport properties. SPPO has higher permselectivities and lower gas permeabilities than PPO. Moreover, membranes formed from an SPPO-methanol solution have a decreased gas permeability compared with the membranes formed from an SPPO-DMA solution. These data indicate that SPPO interactions with methanol and DMA have different natures. SPPO-solvent interactions appear in solution and remain in the membrane.

It was found that SPPO gas transport properties vary with time. The changes are more appreciable for the membranes formed from an SPPO-methanol solution. This effect is caused by the non-equilibrium state of the polymer in newly made membranes.

To summarize, gas transport properties of the SPPO ionomer depend on the solvents used for membrane preparation because the polymer-solvent specific interactions play an important role in formation of the supermolecular order in the polymer.

## THE ORDERING EFFECT AT THE INTERFACE OF POLY-n-FLUOROALKYLACRYLATE/POLYAMIDE-IMIDE COMPOSITE MEMBRANES

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Composite gas separation membranes are usually obtained by the formation on the surface of a microporous polymer support of a thin defect-free layer consisting of a polymer of another chemical nature. The processes occurring at the polymer-polymer interface on passing of the coating polymer from a dilute solution into the condensed state in the membrane formation stage have not been investigated previously. In this area the formation of an ordered supermolecular structure of the coating polymer and essential changing of separation properties of composite membranes are possible.

This suggestion has been confirmed in our study of transport characteristics of composite membranes consisting of microporous asymmetric supports obtained from different polyamide-imides and various coating polymers with a low  $T_g$ .

Characteristic features of the coating polymers used (poly-n -fluoroalkylacrylates and its copolymers) are high segmental mobility of the macromolecules and specific intra- and intermolecular self-organization of polymer chains. By using polyamide-imide homologous series, it was possible to obtain supports with similar morphologies and different free energies of their surfaces.

In the series of membranes investigated when different support polymers were used ( other factors, such as the morphology, the type and the thickness of the coating polymer also are being equal) the separation factor for the  $O_2/N_2$  pair distinguished greatly from 2.6 to 10.0. Similar dependence was observed when only the type of the coating polymer was changed but the morphology and surface properties of the support used remained the same.

Peculiarities of the dependences of separation factors for  $O_2/N_2$  pair on temperature suggest the effects associated with the coating layer structuration.

## MOLECULAR ORDER OF POLYFLUORINATED POLYMERS AND SPECIFIC FEATURES OF THEIR DISSOLUTION PROCESS.

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Polyfluorinated copolymers are promising materials for making selective layers of pervaporation membranes. It is therefore important to study their molecular order in bulk and solutions as this first step in the procedure of preparing thin and ultrathin films from such polymers. The object of this work was an investigation alternating copolymers of ethylene with perfluorinated monomers obtained by emulsion polymerization.

The experiments have demonstrated that

- solubility depends on the time of sample storage after preparation. The freshly synthesized samples form molecular solution in hexafluorobenzene as show the data of the sedimentation analysis. On the contrary, the specimens stored longer than 14 hours contain up to 70 % of gel fraction. Model copolymer of tetrafluoroethylene and ethylene that we have prepared by a published procedure has not shown similar behavior.

- molecular solutions can be obtained from copolymers (even after long storage) in mixed solvents containing small quantities of the additives of compounds which have ability for to specific interaction

These features of the dissolution process can be understood on assumption that the structure of copolymer is microheterogenous, namely, that in the polymer occur areas enriched with hydrocarbon units (hydrocarbon clusters) which form points of physical lattice. The assumption is corroborated by the findings obtained with the help of X-ray study, of light scattering measurements performed on the copolymer solutions and by inversed gas chromatography.

Thus we have demonstrated that polyfluorinated copolymers with the structure close to alternating show microheterogenous packing.

## MODELS OF THE NATURAL POLYMERIC PHOTOSENSITIVE MEMBRANES

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Monolayers of biopolymer-chromophore complexes from pea and spinach have been studied on the air/aqueous interface. These polymers are distinguished by polypeptides content and capable of adsorption on interface. Monolayers of photosystem II (PSII) enriched membranes, core complexes, light-harvesting complex (LHCII) and reaction centers (RC) were investigated in order to determine the influence of protein contents on the monolayer formation on interface. PSII is one of four supramolecular protein complexes, embedded in the thylakoid lipid bilayer, which participate in the flow of electrons from water to  $\text{NADP}^+$ . Monolayers of natural polymer complexes have been prepared. Surface pressure ( $\pi$ ) - area per molecule (A) isotherms of the PSII enriched membranes, LHCII and RC have high collapse pressures (50-53 mN/m) that proves their stability at interface. The areas of RCs and LHCII are in the range of 3.5-4.0 m<sup>2</sup>/mg of proteins and these characteristics of PSII enriched membranes and core complexes monolayers are more less (0.5-0.7 m<sup>2</sup>/mg).  $\pi$ -A isotherms of the core complexes have appeared difference and have smaller collapse pressure (38-42 mN/m). Different types of native lipids were used for modeling of the membrane structure. The dependence of the PSII reaction centers damage in the monolayers at constant surface pressure from light illumination in the presence of oxygen has studied. Monolayer characteristics depended on experimental conditions and lipid contents. These monolayers are useful for modeling of the natural photosensitive membrane and applicable as sensitive thin film for pesticides sensors [1].

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## STRUCTURE AND PROPERTIES OF SULFONATED, STYRENE GRAFTED PVDF MEMBRANES.

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The possibility of developing poly-(vinylidene fluoride), PVDF, based membranes as proton conductors has been investigated. Using electron beam radiation grafting and functionalisation the composition of the membranes can be controlled. Membranes have been prepared from films of PVDE, and their structure and properties have been investigated with Raman spectroscopy, wide angle X-ray scattering, (WAXS), small angle X-ray scattering, (SAXS), swelling tests, and impedance spectroscopy. The grafting reaction, initiated in the amorphous regions and at the surfaces of the crystallites in the partly crystalline PVDE matrix is very efficient, and high degrees of grafting can be achieved. Grafts are formed both from C-H and C-F branch points. Sulfonation can be accomplished to ~100%, and occurs mainly to the para- position of the phenyl rings. The hydration number was found to be independent of degree of grafting, degree of sulfonation and crystallinity. The over-all crystallinity decreased in the structure with degree of grafting and sulfonation, partly due to the dilutive effect of the grafts, partly due to efficient penetration of the grafts in the crystallites. The conductivity increased with the content of sulfonic acid groups, and, in particular, with decreasing crystallinity. In the case of fully sulfonated membranes a leveling out of the conductivity was found at around 200% degree of grafting. Conductivity's up to 120 mS cm<sup>-1</sup> at room temperature were achieved.

## Structure of the Surface Layer of Nanofiltration Membranes

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Nanofiltration has been developed as a novel technology that is especially suitable for separation of multivalent ions and small uncharged molecules with molecular weight more than 300g/mol. Nanofiltration membranes are obtained on a surface of the porous polymeric matrix by interfacial polycondensation using an aqueous solutions of the secondary polyamine and a solution of a polyfunctional acid halide in a water-immiscible organic solvent.

It was known the rigid construction of water transmitting channels from linear or cross-linking polyamide chains, the high local carbonyl concentration and the definite size of channel door holes being formed in the preparation process are the main physico-chemical factors controlling selectivity for H<sub>2</sub>O permeation through barrier layers. Therefore it is extremely important to understand the physico-chemical interactions between main-chain links, their configuration and arrangement.

The experimental samples of nanofiltration selective layers were specially prepared without porous support. A thickness of this films were within the range of 1-5µm. The chemical structure of polyamines and their concentrations were varied.

The morphology of films was determined by analyzing the micrographs of the surface and cross-section made by means of a TEM and SEM. It was shown the films has had a space network structure which consist of the spherical elements 10-30 nm in diameter.

The IR ATR measurements and X-ray Photoelectron Spectroscopy were used to characterize the chemical structure of samples obtained and to calculate a quantity of the cross-linked structural units in the polymer material. It was found the value is about 60-70% depending on the chemical features of used polyamines and its concentration.

The data obtained was compared with a permeability of nanofiltration membranes that were produced on the different polymeric support.

## ON MACROMOLECULAR TRANSFORMATION PECULIARITIES OF "FLOW - FIBER" OF SILKWORM

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A conformational transition of alfa-helix in beta-type is in the base of fiber forming process of natural silk fibroin. This transition is occurred by longitudinal hydrodynamic field interaction in the process of "secret stretch out" of silkworm gland as then stream. Up to this time however, the place of longitudinal field arising, causing of this transition, that is a critical conditions of fiber forming don't determine, because of investigation complications of fibroin behavior into the gland. A study of fibroin behavior is important for silk waste processing.

The silkworm gland is a thin, transparent, tubular construction and to be easy extracted at a caterpillar cutting. And the fiber forming can be carried out afrifically by "secret stretching out". This allowed us to make a polarizational-optical investigations of the "secret" along whale length of the gland.

Methods of study of macromolecule behavior in the longitudinal hydrodynamic field of Frank-Keller and despersion of optical rotation of Moffite-Doty giving information about conformational states of alfa-helical chains, coil, beta-form are used for this aim.

An average rate of "secret stretching out"  $V=1$  sm/s is realized at natural forming of silk fibers. Holding the same rate of the "secret stretching out" we observed an arising of optical anisotropic phase, as a thin stream at joint places of gland departments of "reservoir-coupled removal intestine". At this a value of including degree of fibroin chains is increased from 0,05 till 0,4 that accommodated by rate gradient of longitudinal field  $G = 1000 \cdot 1/6$ .

Experiments on dispersion of optical rotation showed an availability of alfa-helical parts in the chain in the reservoir "secret", beta-structures in the "secret" of coupled removal intestine. After stopping of the "secret stretching out" the beta-structure is preserved. Cutting of the coupled removal intestine showed a transition of liquid stream into gelical one, that is easy lengthening at stretching and fiber forming process is accelerated.

## **RAMAN CHARACTERIZATION OF MACROMOLECULES ORIENTATION IN DRAWN POLYETHYLENES.**

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Raman spectroscopy is an excellent tool for investigation of the polymer structure in terms of chain conformation [1], crystallinity [2] and molecules orientation. Recently, the structure evolution of the polyethylene during the process of drawing, including the initial stages, was investigated [3,4]. However, the quantitative information about macromolecules orientation was not obtained from Raman spectra.

In this work Raman scattering data are used for quantitative characterization of the macromolecules angular distribution along the drawing direction. Polarizations of the incident and scattered light in our experiments were parallel to each other and form the angle  $\alpha$  with the direction of drawing in the sample. We measured the intensities of two Raman lines (1295  $\text{cm}^{-1}$  and 1130  $\text{cm}^{-1}$ ), having different symmetry. An intensity ratio of these lines  $I(1295)/I(1130)$  was used to characterize the degree of macromolecules orientation. It is seen from our experimental data that Raman intensities for different samples is obviously related to a value of the draw ratio. At present, we analyzing these data with aim to determine the half-width of the macromolecules angular distribution function.

The work was supported by grant 96-02-19422 from Russian Foundation for Basic Research.

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## **DETERMINATION OF COMPOSITION OF POLYMER MIXTURES, RANDOM AND BLOCK COPOLYMER BY MEANS GPC METHOD**

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Recently the large attention is given to production of polymer materials with given properties. The application of random and block-copolymers for these purposes permits flexibly to adjust desired characteristics of materials. However, thus problems of correct determination of used copolymers structure and their main characteristics, main of which is composition and compositions heterogeneity are of great importance.

In present work an opportunity of correct application of techniques gel-penetrating chromatography with two detectors (UV and refractometer) is investigated. Objects of research were polymer mixtures, random and block copolymers of styrene and butadiene, and styrene and polydimethylsiloxane.

On the basis of received data a conclusion about impossibility of application of only one detector for correct determination of a copolymer structure due to the existence of strong deviations from the additive law of the response of a detector is made at a different composition of copolymer or polymer mixture. However, due to the existence of "compensation mechanism of deviations" the application of two detectors permits to determine composition with sufficient accuracy. This fact is based on fundamental connection between absorption and light-scattering in polymer solution.

Increase of a relative error of determination of a copolymer composition, received by given method in certain intervals of composition was found. It is connected with hyperbolic character of dependence of the ratio of signals of detectors from a composition. On the basis of that approach, it was found possible to determine applicability and correctness of a given technique for particular chromatographic conditions.

The authors developed program Dual-lgv-v.1-0 for fulfilment of operations and calculations of values and dependencies, used by gel-penetrating chromatographic with double detecting.

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## **MOLECULAR MOBILITY AND STRUCTURING IN FILLED SOLUTIONS AND GELS OF ULTRA HIGH MOLECULAR WEIGHT POLYETHYLENE.**

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The effect of the solvent type, powder filler's nature and concentration on structure, stress-strain properties and relaxation of solutions and gels of ultra high molecular weight polyethylene <UHMWPE> was studied.

It was shown, that UHMWPE solutions represented structuring systems, which flow was spatially dissimilar and was characterized by the availability of flexural yield stress.

Gelation of UHMWPE solutions was determined by local crystallization. Crystallization rate increased as the UHMWPE concentration decreased and as the thermodynamic activity of the solvent increased. The introduction of fillers into gelatinous system caused the shear modules to increase and elasticity modules to decrease.

Crystallization kinetics of filled UHMWPE solutions was studied with the help of differential scanning calorimetry. Solid surface was apt to initiate or to suppress crystallization process in the systems under study depending on structuring conditions.

Filler's nature and concentration also had a pronounced effect on relaxation properties of gelatinous systems.

The influence of temperature and drawing speed on macromolecular network behavior was studied. Gel's structure transformed into highly oriented fibrillar structure, marked by high order and strength, by the action of stretching.

POLYANION-POLYCATION COMPLEXES OF POLYAMMONIUM SALTS WITH  
N,N-DIMETHYL-2-HYDROXYPROPYLENAMMONIUM CHLORIDE  
UNITS IN THE MAIN CHAIN

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*Synopsis*

Some interpolyelectrolyte complexes were obtained between polycations with (N,N-dimethyl-2-hydroxypropylenammonium chloride) units in the main chain and poly(acrylic acid) sodium salt (PANA), on one hand, and poly(2-methyl-2-acrylamidopropane sulfonic acid) sodium salt (PAMPSNa), on the other hand, as polyanions. The cationic polymers were different as concerns both the content of quaternary nitrogen atoms and the degree of branching. The polyanions were different by their structure and also by their molecular weight. The complex formation was followed by the variation of the conductivity and of the specific viscosity of the reaction medium. vs. the unit molar ratio polyanion/polycation.

When the PANA was used as anionic component the deviation of the endpoint from stoichiometry and the aspect of the polyelectrolyte complexes (PEC) were influenced mainly by the polycation structure, the PECs looking like a coacervate as the degree of branching of polycation is increasing. The use of the PAMPSNa as anionic component, whose molecular weight was much higher than of the polycation ( $\sim 10/1$ ), induced the formation of soluble and insoluble PECs, the critical molar ratio between the complementary polyelectrolytes being influenced definitely by the molecular weight of PAMPSNa.

The binding of ionic dyes in the polyanion-polycation complexes was tested with Ponceau 4R as anionic dye in the system polycation/PANA.

# HYDROPHILIC-HYDROPHOBIC NETWORKS CONTAINING POLYDIMETHYLSILOXANE SEQUENCES

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The paper deals with synthesis of hydrophilic - hydrophobic networks based on polydimethylsiloxane (PDMS) and poly(methacrylic acid) (PMAA) sequences with different molecular weights and molar ratios of the PDMS and PMAA segments.

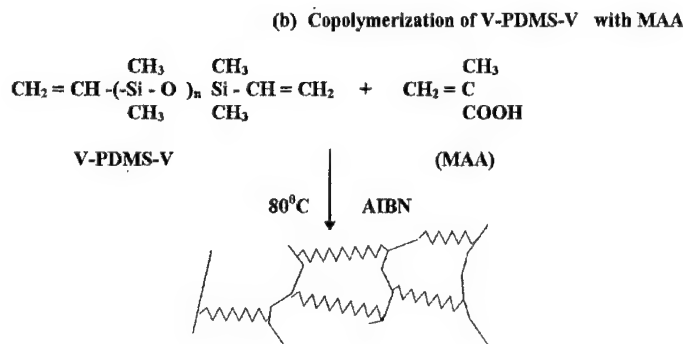
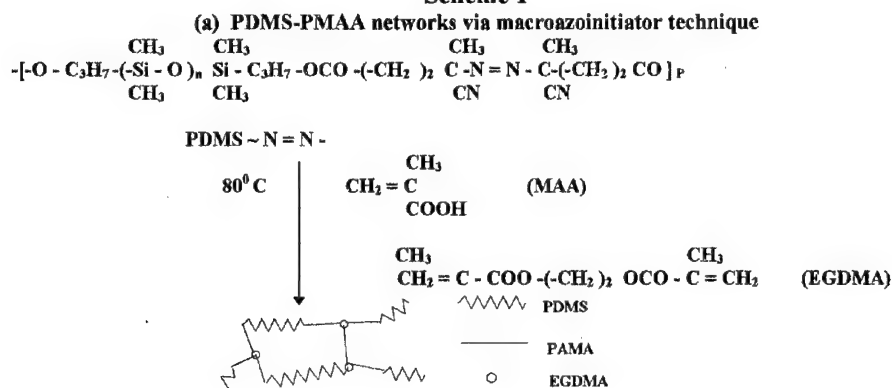
Two methods were used to synthesize the copolymers (Scheme 1):

(a) the radical polymerization of methacrylic acid (MAA) in the presence of dimethylsiloxane macroazoinitiators (-PDMS-N=N-) using ethylene glycol dimethacrylate (EGDMA) as crosslinking agent;

(b) the radical copolymerization of  $\alpha$ ,  $\beta$ -bis(vinylsiloxy)- polydimethylsiloxane (V-PDMS-V) with methacrylic acid, initiated by 2,2'-azobisisobutyronitrile (AIBN).

The structure of the intermediates and of the final products was established by IR and/or NMR spectroscopy. The morphology of the networks was determined by electron microscopy. The synthesized networks proved to present swelling behaviour both in organic solvents and in water.

**Scheme 1**



# **KINETICS OF STRUCTURE DEVELOPMENT IN LIQUID-LIQUID DISPERSIONS UNDER SHEAR FLOW**

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**J.T.Lindt**

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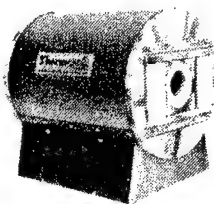
The kinetics of structure development in a moderately concentrated liquid-liquid dispersions under the simple shear flow has been analyzed using differential population balance equations. The existing models of the breakup and coalescence of drops have been examined, modified and included in the population balances to the extent necessary. It was found that in the present range of drop sizes and viscosity ratios the temporal evolution of the average drop size is primarily determined by drop breakup rather than by coalescence. It was further shown that the evolution of the size distribution function as well as the average drop size are strong functions of the viscosity ratio, exhibiting sharp changes at the critical capillary number. The role of the initial drop size distribution on the time-dependent state of the dispersion was examined, including the path leading to a bimodal distribution.

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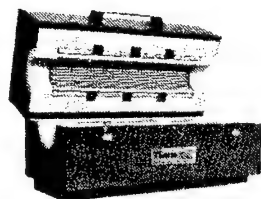
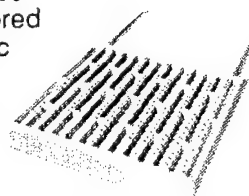


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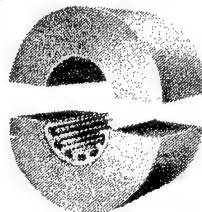


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